

Effective interaction between active colloids and fluid interfaces induced by Marangoni flows

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We show theoretically that near a fluid-fluid interface a single active colloidal particle generating, e.g., chemicals or a temperature gradient experiences an effective force of hydrodynamic origin. This force is due to the fluid flow driven by Marangoni stresses induced by the activity of the particle; it decays very slowly with the distance from the interface, and can be attractive or repulsive depending on how the activity modifies the surface tension. We show that, for typical systems, this interaction can dominate the dynamics of the particle as compared to Brownian motion, dispersion forces, or self-phoretic effects. In the attractive case, the interaction promotes the self-assembly of particles into a crystal-like monolayer at the interface.

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Significant attention has been paid lately to micrometer sized particles capable of self-induced motility [1–3]. They are seen as promising candidates for novel techniques in chemical sensing [4] or water treatment [5]. The motion of active colloidal particles has been the subject of numerous experimental [1–3, 6, 7] and theoretical [8–12] studies. One realization is a particle with a catalytic surface promoting a chemical reaction in the surrounding solution [13]. For an axisymmetric particle lacking fore-and-aft symmetry, the distributions of reactant and product molecules may become non-uniform along its surface and the particle could move due to self-induced phoresis [14]. If the particle is spherically symmetric, it will remain immobile in bulk solution but can be set into motion by the vicinity of walls or other particles (not necessarily active) which break the spherical symmetry [10, 13–16].

A relevant case corresponds to the movement of active particles bounded by a fluid-fluid interface. This situation raises new issues, in particular if the reactants or the products have a significant effect on the properties of the fluid interface implying *tensioactivity*. For example, it has been recently predicted that catalytically active, spherical particles which are trapped *at* the interface may be set into motion *along* the interface by Marangoni flows, self-induced via the spatially non-uniform distribution of tensioactive molecules [17–19]. (A similar motility mechanism can originate from thermally induced Marangoni flows if, e.g., the particle contains a metal cap which is heated by a laser beam [20].) Furthermore, self-induced Marangoni flows, combined with a mechanism of triggering spontaneous symmetry-breaking, have also been used to develop self-propelled droplets [21–23].

However, another category of experimental situations occurs if the particles are not trapped *at* the interface but may *reside in the vicinity* of the interface or *get near* it during their motion. In this study we provide theoretical

evidence that such catalytically active or locally heated spherical particles, although immobile in bulk, experience a very strong, long-ranged effective force field due to the Marangoni stresses self-induced at the interface. This force of hydrodynamic origin manifests itself at spatial length scales much larger than those of typical wetting forces. It gives rise to a drift of the particle towards or away from the fluid interface, depending only on how the tensioactive agent, i.e., a gradient in chemical concentration or in temperature, affects the interface. This effect dominates any possible self-phoresis or dispersion interactions, and acts on time scales which can be orders of magnitude shorter than those associated with Brownian diffusion. This drift can facilitate particle adsorption towards the interface and therefore has important implications for the self-assembly of particles at fluid–fluid interfaces. We complement the theoretical calculations with a thorough analysis regarding the observability of these phenomena in future experiments.

The model system consists of a spherical colloidal particle with radius R in front of a flat interface at $z = 0$ between two immiscible fluids. Fluid 1 (2) occupies the half space $z > 0$ ($z < 0$) (see Fig. 1). The spherical particle is located in fluid 1; its center is at $\mathbf{x}_0 = (0, 0, L)$ with $L > R$, i.e., the particle does not penetrate through the interface. By virtue of a chemical reaction occurring uniformly over its surface [24], the particle acts as a spherically symmetric source (or sink) of a chemical species A . We assume that the time scale for diffusion of A is much shorter than any relevant time scale associated with fluid flows [25]. Therefore we consider only the stationary state neglecting advection by the ensuing Marangoni flow. Additionally, the number density $c(\mathbf{x} = \mathbf{r} + z\mathbf{e}_z)$ of species A (with $\mathbf{r} = (x, y, 0)$ in the following) is assumed to be sufficiently small so that for A the ideal-gas approximation holds, and thus $c(\mathbf{x})$ obeys Fick’s law for

diffusion with diffusivity D_α in fluid α ($= 1, 2$):

$$\nabla^2 c(\mathbf{x}) = 0, \quad \mathbf{x} \in \text{fluid 1 or 2}, \quad (1a)$$

subject to the boundary conditions [25] that (i) a single reservoir of species A fixes the number density far away from the particle to be c_α^∞ in fluid α ($= 1, 2$), (ii) the discontinuity of $c(\mathbf{x})$ at the interface, given by $\lambda := c(\mathbf{r}, z = 0^-)/c(\mathbf{r}, z = 0^+) = c_2^\infty/c_1^\infty$, is determined, as in equilibrium, by the distinct solvabilities of species A in the two fluids, (iii) the current of species A along the direction of the interface normal is continuous at the interface ($D_1 (\partial c / \partial z)|_{z=0^+} = D_2 (\partial c / \partial z)|_{z=0^-}$), and (iv) the current at the surface \mathcal{S}_p of the particle is

$$\mathbf{n} \cdot [-D_1 \nabla c(\mathbf{x})] = \frac{Q}{4\pi R^2}, \quad \mathbf{x} \in \mathcal{S}_p, \quad (1b)$$

where \mathbf{n} is the unit vector normal to \mathcal{S}_p (pointing into fluid 1); $Q > 0$ ($Q < 0$) is the rate of production (annihilation) of species A .

The surface tension γ of the fluid interface is assumed to depend on the local number density of species A and is modeled within the local equilibrium approximation as [25]

$$\gamma(\mathbf{r}) = \gamma_0 - b_0 [c(\mathbf{r}, z = 0^+) - c_1^\infty]. \quad (2)$$

Here, γ_0 is the surface tension in equilibrium in which the density of A in fluid 1 is c_1^∞ ; the effect of local deviations thereof are quantified by the coefficient b_0 , the sign of which depends on the chemical.

This inhomogeneity of the surface tension induces Marangoni stresses which set the fluids into motion. The velocity field $\mathbf{v}(\mathbf{x})$ can be derived as solution of the Stokes equations (i.e., in the limit of incompressible flow and negligible inertia):

$$\nabla \cdot \mathbf{v}(\mathbf{x}) = 0, \quad \nabla \cdot \overset{\leftrightarrow}{\sigma}(\mathbf{x}) = 0, \quad \mathbf{x} \in \text{fluid 1, 2}, \quad (3a)$$

where $\overset{\leftrightarrow}{\sigma}(\mathbf{x}) = \eta(\mathbf{x})[\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger] - p(\mathbf{x})\mathcal{I}$ is the stress tensor in the fluid, $p(\mathbf{x})$ the pressure, $\eta(\mathbf{x})$ the viscosity, and \mathcal{I} denotes the second-rank identity tensor. The Stokes equations are subject to the following boundary conditions: (i) vanishing velocity at infinity, (ii) no slip flow at the surface of the particle, (iii) at the interface, continuity of the tangential velocity and vanishing of the normal velocity, and (iv) balance between the tangential fluid stresses and the Marangoni stresses induced by the gradient of the surface tension along the interface:

$$(\mathcal{I} - \mathbf{e}_z \mathbf{e}_z) \cdot \left[\overset{\leftrightarrow}{\sigma} \Big|_{z=0^+} - \overset{\leftrightarrow}{\sigma} \Big|_{z=0^-} \right] \cdot \mathbf{e}_z = -\nabla_\parallel \gamma. \quad (3b)$$

The tensor $(\mathcal{I} - \mathbf{e}_z \mathbf{e}_z)$ provides the projection onto the interfacial plane and $\nabla_\parallel = (\partial_x, \partial_y, 0)$ is the nabla operator within the interfacial plane. (Actually, the interface must deform so that the normal component of the fluid

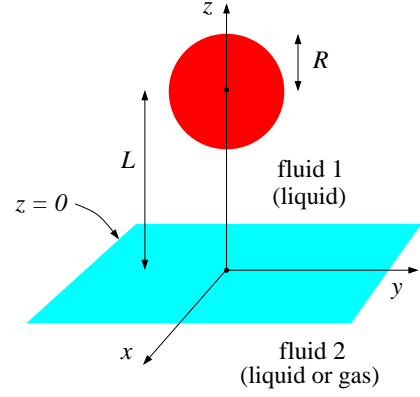


FIG. 1. Coordinates and configuration of the system. The interface between fluid 1 (liquid) and fluid 2 (liquid or gas) is located at $z = 0$.

stresses can be balanced by the Laplace pressure. *A posteriori* it turns out [25] that this deformation is typically so small that the flat interface approximation is reliable.)

The translation velocity \mathbf{V} of the particle, or equivalently the force \mathbf{F} exerted by the particle on the fluid, can be inferred from the Lorentz reciprocal theorem [32]. We consider the auxiliary flow field $\mathbf{v}_{\text{aux}}(\mathbf{x})$, for the same geometrical setup, corresponding to the translation of a rigid, spherical, *chemically passive* (i.e., without Marangoni stresses) particle in front of a flat fluid interface. This is the solution of Eq. (3a) subject to the same boundary conditions as above but with $\nabla_\parallel \gamma = 0$ in Eq. (3b), a problem studied in Refs. [33–35]. We thus obtain [25]

$$\begin{aligned} \mathbf{F}_{\text{aux}} \cdot \mathbf{V} - \mathbf{V}_{\text{aux}} \cdot \mathbf{F} &= \int_{z=0} d^2 \mathbf{r} \nabla_\parallel \gamma(\mathbf{r}) \cdot \mathbf{v}_{\text{aux}}(\mathbf{r}) \\ &= - \oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \overset{\leftrightarrow}{\sigma}_{\text{aux}}(\mathbf{x}) \cdot \mathbf{u}(\mathbf{x}), \end{aligned} \quad (4)$$

with

$$\mathbf{u}(\mathbf{x}) = \int_{z=0} d^2 \mathbf{r}' \nabla_\parallel \gamma(\mathbf{r}') \cdot \mathcal{O}(\mathbf{x} - \mathbf{r}') \quad (5a)$$

in terms of the Oseen tensor,

$$\mathcal{O}(\mathbf{x}) = \frac{1}{8\pi\eta_+ x} \left[\mathcal{I} + \frac{\mathbf{x}\mathbf{x}}{x^2} \right], \quad \eta_+ := \frac{1}{2}(\eta_1 + \eta_2). \quad (5b)$$

Here, $\mathbf{u}(\mathbf{x})$ is the Marangoni flow, which would be induced solely by the Marangoni stresses $\nabla_\parallel \gamma(\mathbf{r})$, i.e., as if the surface of the particle would not impose any boundary condition on the flow [25]. Note that Eq. (4) can be interpreted as a generalization of the Faxén laws [36] for the present problem. For a force-free ($\mathbf{F} = 0$ in Eq. (4)) spherical particle, the problem exhibits axial symmetry, which implies that \mathbf{V} is parallel to \mathbf{e}_z . Thus, it suffices to solve the auxiliary problem with $\mathbf{F}_{\text{aux}} \parallel \mathbf{e}_z$, which allows one to introduce the dimensionless stream function

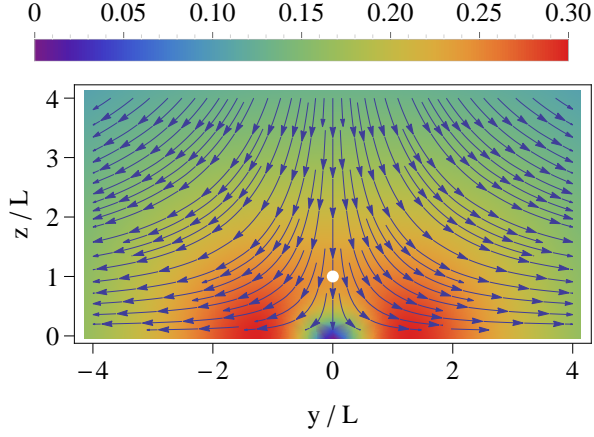


FIG. 2. Vertical cut through the Marangoni flow $\mathbf{u}(\mathbf{x})$ in the limit $R/L \rightarrow 0$ (Eq. (8)). The streamlines follow the direction of the vector field (assuming $Qb_0 > 0$), while the color code corresponds to $|\mathbf{u}(\mathbf{x})|$ in units of $|Qb_0|/(16\pi D_+ \eta_+ L)$. The center of the particle (white dot) is at $y = 0, z/L = 1$. The three-dimensional flow field is obtained by rotation around the z -axis and mirror reflection with respect to the interfacial plane $z = 0$. (This flow is driven by the stress located at the interface, not by the particle.)

$\psi_{\text{aux}}(r, z)$, in terms of which Eq. (4) reduces to [25]

$$\mathcal{V} = -\mathbf{e}_z 2\pi R^2 b_0 \Gamma_z \int_0^\infty dr \left. \frac{\partial c}{\partial r} \right|_{z=0^+} \left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0}, \quad (6)$$

where Γ_z is the L -dependent mobility of a (chemically passive) rigid spherical particle moving normal to the planar fluid interface [35].

The boundary-value problems given by Eqs. (1) and (3), subject to the coupling provided by Eq. (2), can be solved exactly as a series in terms of bipolar coordinates [25]. However, the relevant phenomenology can be highlighted and significant physical intuition can be gained from an approximate closed form valid asymptotically in the limit $R/L \rightarrow 0$. We therefore proceed with the latter; its range of validity will be assessed later by comparison with the exact solution (see, c.f., Fig. 3).

To lowest order in R/L , the solution of Eq. (1) for the given boundary conditions can be obtained using the method of images in terms of monopoles located at $\mathbf{x}_0 = (0, 0, L)$ and $\mathbf{x}_0^* = (0, 0, -L)$. In fluid 1 ($z > 0$) one has

$$c(\mathbf{x}) = c_1^\infty + \frac{Q}{4\pi D_1} \left[\frac{1}{|\mathbf{x} - \mathbf{x}_0|} + \frac{D_1 - \lambda D_2}{D_1 + \lambda D_2} \frac{1}{|\mathbf{x} - \mathbf{x}_0^*|} \right]. \quad (7)$$

Accordingly, the Marangoni flow (illustrated in Fig. 2) is given by Eqs. (2) and (5a) as $\mathbf{u}(\mathbf{x}) = \mathbf{e}_z u_z(r, z) + \mathbf{e}_r u_r(r, z)$ with [25]

$$u_z(r, z) = -\frac{Qb_0}{16\pi D_+ \eta_+} \frac{z(|z| + L)}{[r^2 + (|z| + L)^2]^{3/2}}, \quad (8a)$$

$$u_r(r, z) = \frac{Qb_0}{16\pi D_+ \eta_+ r} \left[1 - \frac{r^2 L + (|z| + L)^3}{[r^2 + (|z| + L)^2]^{3/2}} \right], \quad (8b)$$

and $D_+ := (D_1 + \lambda D_2)/2$. The integral over \mathcal{S}_p in the second line of Eq. (4) can be evaluated by expanding the Marangoni flow in terms of a Taylor series about the particle center so that asymptotically $\mathbf{u}(\mathbf{x}) \approx \mathbf{u}(\mathbf{x}_0)$ for $R/L \rightarrow 0$. Since $\oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \vec{\sigma}_{\text{aux}}(\mathbf{x}) = -\mathbf{F}_{\text{aux}}$, and \mathbf{F}_{aux} can be chosen arbitrarily, one concludes that a force-free ($\mathbf{F} = 0$) active particle at a distance L from the interface is carried by the flow with velocity

$$\mathcal{V}(L) \approx \mathbf{u}(\mathbf{x}_0) \approx -\mathbf{e}_z \frac{Qb_0}{64\pi D_+ \eta_+ L} \quad (9)$$

due to the self-induced Marangoni stresses. Since $\mathcal{V} \parallel \mathbf{e}_z$, this implies a time dependence of L .

Equation (9) captures the essence of all the relevant phenomenology. (i) For $b_0 > 0$ (i.e., the generic surfactant case) the particle drifts towards or away from the interface if it is a source ($Q > 0$) or a sink ($Q < 0$) of species A , respectively. For $b_0 < 0$, the behavior is reversed. (ii) The slow $1/L$ decay of \mathcal{V} is tantamount to a long-ranged interaction with the fluid interface. The associated phenomenology can dominate the influence of dispersion forces between the particle and the interface, which decay $\sim 1/L^4$ at best [37], and also the motion due to Brownian diffusion alone.

The argument can be quantified by introducing the diffusion coefficient $D_p := k_B T / (6\pi \eta_+ R)$ of the particle in a medium of viscosity η_+ at temperature T . Equation (9) leads to the Peclet number of the particle

$$\text{Pe}(L) := \frac{R|\mathcal{V}(L)|}{D_p} = |q| \frac{R}{L}, \quad q := \frac{3Qb_0 R}{32D_+ k_B T}. \quad (10)$$

Dominance of drift means $\text{Pe}(L) \gtrsim 1$. Thus, one estimates the distance L_{max} from the interface, beyond which the motion of the particle is controlled by diffusion rather than by drift, as $\text{Pe}(L_{\text{max}}) = 1$ so that $L_{\text{max}} = |q|R$. Focusing on the case $b_0 > 0$, one can determine the time t_{drift} it takes the particle to reach the interface starting (for $Q > 0$) from a given distance L_0 (or, for $Q < 0$, to reach a given distance L_0 starting from near the interface) via straightforward integration of the equation of motion $dL/dt = \mathbf{e}_z \cdot \mathcal{V}$ (within the overdamped regime [25]). This renders the drift time $t_{\text{drift}} = t_{\text{diff}}/(2|q|)$ in terms of the time of diffusion $t_{\text{diff}} := L_0^2/D_p$ over the same distance L_0 . Therefore, for large values of $|q|$ the drift caused by the Marangoni flow, rather than diffusion, dominates the dynamics of the particle.

In order to estimate the magnitude of q , we shall use that typically b_0 can take values in the range from $b_0 \sim -10^{-3} \text{ N}/(\text{m} \times \text{M})$ (M denotes mol/liter) for simple inorganic salts in water [38], up to $b_0 \sim 10^2 \text{ N}/(\text{m} \times \text{M})$ for dilute solutions of surfactants (i.e., far from their critical micelle concentrations) [39]. We consider two distinct

set-ups of potential experimental relevance.

(i) The particle is a source. The chemical species A is molecular oxygen liberated from peroxide in aqueous solution by a platinum-covered particle. For the experimental conditions described in Ref. [40], one has $Q/(4\pi R^2) \approx 10^{-3} \text{ mol}/(\text{s} \times \text{m}^2)$ (compare Eq. (1b)). At room temperature (300 K) and for $R \simeq 1 \mu\text{m}$, Eq. (10) leads to $|q| \sim 3 \times 10^{-4} \times (D_+/(m^2 \times s^{-1}))^{-1} (|b_0|/(N \times m^{-1} \times M^{-1}))$. For an air (fluid 2)–water (fluid 1) interface [41], diffusion in the gas phase dominates (typically $D_2 \simeq 10^{-5} \text{ m}^2/\text{s}$ and $D_1 \simeq 10^{-9} \text{ m}^2/\text{s}$ [42]), and $D_+ \approx \lambda D_2/2 \simeq 10^{-4} \text{ m}^2/\text{s}$ (since $\lambda \sim 10 - 100$ for oxygen and air–water interface [43]), while b_0 is in the lower range of values [40]. Thus $L_{\text{max}}/R = |q| \sim 10^{-2}$, which explains the lack of reports of such effects for experimental set-ups as in Ref. [40]. However, for a liquid–liquid interface (e.g., water–decane), one has $D_+ \simeq D_1 \simeq D_2 \simeq 10^{-9} \text{ m}^2/\text{s}$ (one expects $\lambda \lesssim 1$ [42]) and thus $|q| \gtrsim 10^2$ across the range of values b_0 noted above. Therefore, for the same experimental set-ups of active colloids, but which involve liquid–liquid interfaces instead of liquid–gas ones, we predict that the effective interactions discussed here dominate. The same conclusion holds for liquid–gas interfaces but with a reaction product with very low solubility in the gas phase (i.e., $\lambda \ll 1$).

(ii) The particle is a sink, i.e., the tensioactive species A is absorbed completely by the particle. One can infer Q from the diffusion-limited regime in which the surface of the particle acts as an absorbing boundary so that $c(\mathbf{x} \in \mathcal{S}_p) = 0$, which with Eq. (7) provides the estimate $Q \approx -4\pi D_1 R c_1^\infty$ as $R/L \rightarrow 0$. With Eq. (10) one arrives at $|q| \sim 3 \times 10^8 \times (D_1/D_+)(R/\mu\text{m})^2 (c_1^\infty/M) (|b_0|/(N \times m^{-1} \times M^{-1}))$. Therefore, $L_{\text{max}}/R = |q|$ can indeed be large for colloidal particles even if species A is only weakly tensioactive (i.e., $|b_0|$ small) and even for liquid–gas interfaces ($D_1/D_+ \ll 1$).

The availability of an exact series representation for \mathcal{V} as given by Eq. (6) allows us to assess the range of validity of the asymptotic approximation (Eq. (9)) discussed above. For several values of the viscosity and diffusivity ratios [25], Fig. 3 shows $\mathcal{V}/u(\mathbf{x}_0)$ as a function of the separation L/R . It turns out that $u(\mathbf{x}_0)$ provides a reliable approximation (less than 10% relative error) of the exact solution down to separations $L/R \simeq 2$, i.e., covering most of the range within which the model is relevant. Furthermore, the deviations from $u(\mathbf{x}_0)$ depend very weakly on the ratios η_2/η_1 and $\lambda D_2/D_1$.

These results, yet to be explored experimentally, have several implications, which we highlight in conclusion. First, as noted in the Introduction, if the particle maintains a temperature gradient, e.g., through local heating, the very same equations hold with the temperature playing the role of the number density $c(\mathbf{x})$. Therefore, all the phenomenology discussed above extends to this case, too. Second, sufficiently close to the interface the drift due to the induced Marangoni flows can dominate even

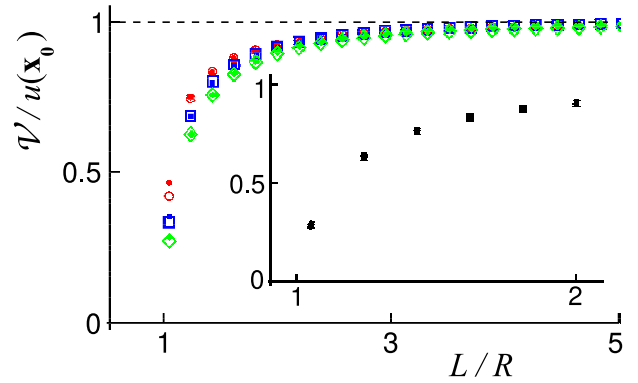


FIG. 3. The ratio $\mathcal{V}/u(\mathbf{x}_0)$ (Eqs. (6) and (9)) as a function of L/R for $\lambda D_2/D_1 = 0.1, 1, 10$ (\circ, \square, \diamond) and $\eta_2/\eta_1 = 0.1, 10$ (open, filled). The inset provides an enlarged view of the range $L/R \lesssim 2$ for $\lambda D_2/D_1 = 10$ and $\eta_2/\eta_1 = 0.02, 0.1, 1, 10, 50$ ($\circ, \square, \diamond, \triangle, \times$); at that scale, the data are indistinguishable. The dashed line indicates the approximation provided by Eq. (9).

self-phoretic motion. For instance, a Janus particle of size $R = 1 \mu\text{m}$ (with $D_p \sim 10^{-13} \text{ m}^2/\text{s}$ in water) and self-propelling with a typical velocity of $\sim 1 \mu\text{m}/\text{s}$ [1] has a Peclet number $\text{Pe}_{\text{phor}} \simeq 10$, which, e.g., at distances $L/R < 10$ is smaller than $\text{Pe}(L) = (R/L)|q|$ if $|q| \gtrsim 10^2$ (see Eq. (10)). Third, based on the single-particle phenomenology studied here one can infer potentially significant collective effects. Consider for example a dilute suspension of active particles which are driven towards the interface by the Marangoni stresses and in addition experience a short-ranged repulsion by the interface (e.g., due to electrostatic double layer interactions). Then the particles are expected to reside near the interface while experiencing a mutual long-ranged lateral repulsion as each particle is carried by the Marangoni flows induced by the others (see the flow lines in Fig. 2 and Eq. (8b), which tells that u_r exhibits also a slow in-plane decay $\sim 1/r$). Therefore, near the interface and in the presence of lateral boundaries self-organized crystal-like monolayers could be reversibly assembled and “dissolved” by simply turning on and off the activity of the particles. Finally, we note that this effective lateral pair interaction violates the action-reaction principle because non-identical particles (e.g., due to size-polydispersity, different production rates Q , or a heterogeneous coverage of the surface) create Marangoni flows of different strength. As for other systems in which such violations occur [44], this feature can be expected to give rise to a complex collective behavior and to a rich, barely explored phenomenology.

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SUPPLEMENTARY INFORMATION

CONTENTS

I. The boundary–value problem posed in Eq. (1)	1
II. The dependence of the surface tension on the field $c(\mathbf{x})$	2
III. Derivation of Eqs. (4-6) in the main text	3
IV. Derivation of Eqs. (7) and (8) in the main text	5
V. Exact solution for the velocity \mathbf{v}	7
A. Solution of the diffusion equation	7
B. Solution of the auxiliary problem in terms of bipolar coordinates	8
C. Calculation of the drift velocity \mathbf{v} in terms of bipolar coordinates	13
D. Derivation of Eq. (V.37)	14
VI. Particle drift induced by Marangoni flow	15
VII. Consistency of the applied approximations	15
References	17

I. THE BOUNDARY–VALUE PROBLEM POSED IN EQ. (1)

With the hypothesis that the time scale for diffusion of species A is sufficiently short (see Sec. VII), the stationary spatial distribution $c(\mathbf{x})$ of species A can be obtained by assuming local equilibrium. This allows one to define a local free energy, depending on temperature and the local number density $c(\mathbf{x})$, as well as the corresponding chemical potential $\mu(c(\mathbf{x}))$. (Here, the temperature dependence of μ is not explicitly indicated because we shall focus on isothermal systems.) The chemical potential can be decomposed, as usual, into an ideal gas contribution and an excess part which includes, among other terms, the potential energy U_α per A molecule immersed in the background fluid α (i.e., the solvability of A in α). Since the latter depends on the fluid α , we write the chemical potential $\mu(c(\mathbf{x}))$ as $\mu_\alpha(c(\mathbf{x}))$, $\alpha = 1, 2$. Therefore, $c(\mathbf{x})$ is the solution of the following boundary value problem:

$$\nabla \cdot \mathbf{j}_\alpha = 0, \quad \mathbf{j}_\alpha(\mathbf{x}) := -\Gamma_\alpha c(\mathbf{x}) \nabla \mu_\alpha(c(\mathbf{x})), \quad \text{if } \mathbf{x} \in \text{fluid } \alpha = 1, 2, \quad (\text{I.1a})$$

$$\mu_\alpha(c(\mathbf{x})) \rightarrow \mu_0, \quad \text{if } |\mathbf{x}| \rightarrow \infty, \quad (\text{I.1b})$$

$$\mu_1(c(\mathbf{r}, z = 0^+)) = \mu_2(c(\mathbf{r}, z = 0^-)), \quad \text{at the interface } z = 0, \quad (\text{I.1c})$$

$$\mathbf{e}_z \cdot [\mathbf{j}_1(\mathbf{r}, z = 0^+) - \mathbf{j}_2(\mathbf{r}, z = 0^-)] = 0, \quad \text{at the interface } z = 0, \quad (\text{I.1d})$$

$$\mathbf{n} \cdot \mathbf{j}_1(\mathbf{x}) = \frac{Q}{4\pi R^2}, \quad \text{if } \mathbf{x} \in \mathcal{S}_p. \quad (\text{I.1e})$$

Here, Eq. (I.1a) is Fick's law for the particle current density $\mathbf{j}(\mathbf{x})$, expressed in terms of the chemical potential and the mobility Γ_α of species A in the fluid α . Eq. (I.1b) fixes the chemical potential of species A far from the colloidal particle to be that of the reservoir, i.e., μ_0 . This determines the number densities c_1^∞ and c_2^∞ in the fluids far from the particle:

$$\mu_1(c_1^\infty) = \mu_2(c_2^\infty) = \mu_0. \quad (\text{I.2})$$

Equation (I.1c) represents the condition of (local) equilibrium at the interface and determines the jump in $c(\mathbf{x})$ at the interface. Equation (I.1d) expresses the continuity of the normal component of the current of A molecules through the interface, so that there is no accumulation of species A there. Finally, Eq. (I.1e) accounts for the colloidal particle being a source (or sink) of species A .

In order to be able to obtain an analytical solution of this boundary-value problem a specific expression for the chemical potential of species A as a function of the number density c is needed. For reasons of simplicity, we consider the dilute limit, so that for A the ideal-gas approximation can be used. This implies

$$\mu_\alpha(c) = k_B T \ln \frac{c}{c_0} + U_\alpha, \quad \alpha = 1, 2. \quad (\text{I.3})$$

Here, c_0 is a constant reference number density and U_α is the effective potential energy of a molecule A immersed in the fluid α . A nonzero value of the difference $U_1 - U_2$ indicates different solvabilities of A in the two fluids. With this expression for the chemical potential, the current density takes the form

$$\mathbf{j}_\alpha(\mathbf{x}) = -D_\alpha \nabla c(\mathbf{x}), \quad D_\alpha := k_B T \Gamma_\alpha, \quad (\text{I.4})$$

where D_α is the diffusivity of species A in fluid α , which in the dilute limit is spatially constant. Correspondingly, the boundary-value problem (I.1) reduces to

$$\nabla^2 c = 0, \quad \text{if } \mathbf{x} \in \text{fluid 1 or 2}, \quad (\text{I.5a})$$

$$\lim_{|\mathbf{x}| \rightarrow \infty} c(\mathbf{x}) = \begin{cases} c_1^\infty := c_0 e^{(\mu_0 - U_1)/k_B T}, & z > 0, \\ c_2^\infty := c_0 e^{(\mu_0 - U_2)/k_B T}, & z < 0, \end{cases} \quad (\text{I.5b})$$

$$\lambda := \frac{c(\mathbf{r}, z = 0^-)}{c(\mathbf{r}, z = 0^+)} = e^{(U_1 - U_2)/k_B T} = \frac{c_2^\infty}{c_1^\infty}, \quad \text{at the interface } z = 0, \quad (\text{I.5c})$$

$$D_1 \left. \frac{\partial c}{\partial z} \right|_{z=0^+} = D_2 \left. \frac{\partial c}{\partial z} \right|_{z=0^-}, \quad \text{at the interface } z = 0, \quad (\text{I.5d})$$

$$\mathbf{n} \cdot [-D_1 \nabla c(\mathbf{x})] = \frac{Q}{4\pi R^2}, \quad \text{if } \mathbf{x} \in S_p, \quad (\text{I.5e})$$

where we have introduced the ratio λ which characterizes the discontinuity of the field $c(\mathbf{x})$ at the interface (above the molecular scale). In this manner, Eq. (1) and the corresponding boundary conditions (i–iv) in the main text are obtained. The exact solution of this system of equations will be provided in Sec. V A.

II. THE DEPENDENCE OF THE SURFACE TENSION ON THE FIELD $c(\mathbf{x})$

The surface tension γ of the fluid interface depends on the structural properties of both fluid phases, in particular on the number density of species A in each of them. In the absence of particle activity (i.e., $Q = 0$ in Eq. (I.1e)), the solution of Eq. (I.1) is the equilibrium state with

$$\mu_1(c(\mathbf{x})) = \mu_2(c(\mathbf{x})) = \mu_0, \quad \forall \mathbf{x} \quad \Rightarrow \quad c(\mathbf{x}) = \begin{cases} c_1^\infty, & \mathbf{x} \in \text{fluid 1}, \\ c_2^\infty, & \mathbf{x} \in \text{fluid 2}, \end{cases} \quad (\text{II.1})$$

which is a homogeneous distribution of species A in each fluid. The surface tension of the interface in this state is denoted as γ_0 . A variation $\delta\mu_0$ of the chemical potential of the reservoir induces changes δc_1 and δc_2 of the number densities of A in the two fluids. They follow from Eqs. (II.1) and (I.2) as

$$\delta c_1 \frac{\partial \mu_1}{\partial c_1} (c_1 = c_1^\infty) = \delta c_2 \frac{\partial \mu_2}{\partial c_2} (c_2 = c_2^\infty), \quad (\text{II.2})$$

by retaining only the lowest order terms in the deviations. The corresponding change in the surface tension is taken into account consistently to lowest order in the deviations:

$$\gamma = \gamma_0 - b_0 \delta c_1 = \gamma_0 - \hat{b}_0 \delta c_2, \quad b_0 := -\frac{d\gamma}{dc_1}(c_1 = c_1^\infty), \quad \hat{b}_0 := -\frac{d\gamma}{dc_2}(c_2 = c_2^\infty). \quad (\text{II.3})$$

Here, the coefficient b_0 quantifies the effect of the deviations in c_1 and it encodes the effective molecular interactions between the A molecules and the interface between the two fluids. We note that the variations in γ can be expressed equivalently in terms of quantities pertaining only to fluid 2, because the equilibrium condition determines unambiguously the relationship between the densities of A on each side of the interface: from Eq. (II.2) one has the relationship

$$\frac{1}{b_0} \frac{\partial \mu_1}{\partial c_1}(c_1 = c_1^\infty) = \frac{1}{\hat{b}_0} \frac{\partial \mu_2}{\partial c_2}(c_2 = c_2^\infty). \quad (\text{II.4})$$

If the particle is active, the distribution of species A is described by a nonequilibrium, spatially varying state. In such a case, the surface tension of the interface is determined by considering local equilibrium: Eq. (II.3) holds but with the deviation δc_1 given locally by the difference $c(\mathbf{r}, z = 0^+) - c_1^\infty$. This yields Eq. (2) in the main text.

III. DERIVATION OF EQS. (4-6) IN THE MAIN TEXT

The Lorentz reciprocal theorem [1, 2] for the Stokes equation in the domain \mathcal{D} outside the particle, which is bounded by the surface \mathcal{S}_p of the particle and a surface \mathcal{S}_∞ at infinity, takes the form

$$\oint_{\mathcal{S}_p \cup \mathcal{S}_\infty} dS \mathbf{n}_{\text{out}} \cdot \overleftrightarrow{\sigma}_{\text{aux}} \cdot \mathbf{v} - \int_{\mathcal{D}} d^3\mathbf{x} (\nabla \cdot \overleftrightarrow{\sigma}_{\text{aux}}) \cdot \mathbf{v} = \oint_{\mathcal{S}_p \cup \mathcal{S}_\infty} dS \mathbf{n}_{\text{out}} \cdot \overleftrightarrow{\sigma} \cdot \mathbf{v}_{\text{aux}} - \int_{\mathcal{D}} d^3\mathbf{x} (\nabla \cdot \overleftrightarrow{\sigma}) \cdot \mathbf{v}_{\text{aux}}, \quad (\text{III.1})$$

where \mathbf{n}_{out} denotes the unit vector normal to the bounding surface and oriented towards the exterior of the fluid (the so-called *outer normal*). The flow field $\mathbf{v}(\mathbf{x})$ in Eq. (III.1) corresponds to our model describing an active rigid particle which moves with velocity \mathbf{V} in front of a fluid interface (in the Monge representation $z = f(x, y)$ characterized by a function $f(\mathbf{r})$ of the lateral coordinates $\mathbf{r} := (x, y, 0)$) with a local surface tension $\gamma(\mathbf{r})$, and is thus given as the solution of the boundary-value problem

$$\nabla \cdot \mathbf{v} = 0, \quad \nabla \cdot \overleftrightarrow{\sigma} = -\delta(z - f(x, y)) [\nabla_{\parallel} \gamma + 2\gamma H \mathbf{e}_n], \quad \text{if } \mathbf{x} \in \mathcal{D}, \quad (\text{III.2a})$$

$$\mathbf{v}(\mathbf{x}) \text{ continuous everywhere}, \quad (\text{III.2b})$$

$$\mathbf{e}_n \cdot \mathbf{v} = 0 \text{ at the interface } z = f(x, y), \quad (\text{III.2c})$$

$$\mathbf{v}(\mathbf{x}) = \mathbf{V}, \quad \text{if } \mathbf{x} \in \mathcal{S}_p, \quad (\text{III.2d})$$

$$\mathbf{v}(|\mathbf{x}| \rightarrow \infty) = 0, \quad (\text{III.2e})$$

$$\overleftrightarrow{\sigma} := \eta(\mathbf{x}) [\nabla \mathbf{v} + (\nabla \mathbf{v})^\dagger] - p \mathcal{I}. \quad (\text{III.2f})$$

With $p = f_x$, $q = f_y$, $r = f_{xx}$, $s = f_{xy}$, and $t = f_{yy}$, here $\mathbf{e}_n(x, y) := (-p, -q, 1)/\sqrt{1 + p^2 + q^2}$ denotes the local unit vector normal to the interface and $H(x, y) = [r(1 + q^2) - 2pq s + t(1 + p^2)]/[2(1 + p^2 + q^2)^{3/2}]$ is its local mean curvature. The effect of the interface on the flow is incorporated through Eq. (III.2a) (via the Marangoni stress $\nabla_{\parallel} \gamma$ and the Laplace pressure $2\gamma H$, respectively) and Eq. (III.2c) (via the kinematic constraint of a stationary interface). The hydrodynamic flow deforms the shape of the interface relative to its flat configuration such that the Laplace pressure $2\gamma H$ due to the deformation can balance the pull by the flow, i.e., the difference in normal stresses across the interface. Thus the deformation $f(x, y)$ would be computed as part of the solution of the boundary-value problem. However, the relatively large value of the surface tension in typical set-ups implies that the deformation is usually small and the interface is close to the plane $z = 0$ everywhere. Therefore one can approximate the initial problem by assuming the interface to be flat in the geometric sense (formally $f \rightarrow 0$, which means that the deformations are

negligible compared to all other relevant length scales), but subject to an in-plane stress given by $\nabla_{\parallel}\gamma(\mathbf{r})$ and subject to an unknown areal density of force $\mathbf{e}_z\phi(\mathbf{r})$ which imposes the flat-interface constraint. The latter can be interpreted as the formal limit $2\gamma(\mathbf{r})H(\mathbf{r})\mathbf{e}_n \rightarrow \phi(\mathbf{r})\mathbf{e}_z$, $\phi(\mathbf{r})$ finite, of the Laplace pressure, if $H \rightarrow 0$ and $\gamma \rightarrow \infty$. This leads to the simplified boundary-value problem

$$\nabla \cdot \mathbf{v} = 0, \quad \nabla \cdot \overset{\leftrightarrow}{\sigma} = -\delta(z) [\nabla_{\parallel}\gamma + \mathbf{e}_z\phi], \quad \text{if } \mathbf{x} \in \mathcal{D}, \quad (\text{III.3a})$$

$$\mathbf{v}(\mathbf{x}) \text{ continuous everywhere}, \quad (\text{III.3b})$$

$$\mathbf{e}_z \cdot \mathbf{v} = 0 \text{ at the interface } z = 0, \quad (\text{III.3c})$$

$$\mathbf{v}(\mathbf{x}) = \mathbf{V}, \quad \text{if } \mathbf{x} \in \mathcal{S}_p, \quad (\text{III.3d})$$

$$\mathbf{v}(|\mathbf{x}| \rightarrow \infty) = 0, \quad (\text{III.3e})$$

$$\overset{\leftrightarrow}{\sigma} := \eta(\mathbf{x}) [\nabla \mathbf{v} + (\nabla \mathbf{v})^{\dagger}] - p\mathcal{I}, \quad (\text{III.3f})$$

which is the boundary-value problem formulated in Eq. (3) in the main text. (In particular, Eq. (3b) is obtained by integrating Eq. (III.3a) over an infinitesimal cylindrical box (centered at the interface with its axis parallel to the interface normal \mathbf{e}_z), applying Gauss' theorem, and then taking the in-plane projection of the result.) This problem can be solved without the need to apply the stress balance boundary condition at the interface in normal direction arising from Eq. (III.3a), because the interface shape is prescribed and fixed to be planar. The constraining force ϕ follows from the discontinuity in the normal stress at the interface *after* the solution has been found. Then ϕ can be used to estimate the curvature as $H(\mathbf{r}) = \phi(\mathbf{r})/(2\gamma(\mathbf{r}))$. This allows one to check *a posteriori* the self-consistency of the flat-interface approximation (see Sec. VII).

As for $\mathbf{v}_{\text{aux}}(\mathbf{x})$, we choose it to be the flow field for the same geometry (within the same flat-interface approximation discussed above) but for a passive particle, i.e., in the absence of Marangoni flow. Thus $\mathbf{v}_{\text{aux}}(\mathbf{x})$ is the solution of Eq. (III.3) but with $\nabla_{\parallel}\gamma = 0$:

$$\nabla \cdot \mathbf{v}_{\text{aux}} = 0, \quad \nabla \cdot \overset{\leftrightarrow}{\sigma}_{\text{aux}} = -\delta(z)\mathbf{e}_z\phi_{\text{aux}}, \quad \text{if } \mathbf{x} \in \mathcal{D}, \quad (\text{III.4a})$$

$$\mathbf{v}_{\text{aux}}(\mathbf{x}) \text{ continuous everywhere}, \quad (\text{III.4b})$$

$$\mathbf{e}_z \cdot \mathbf{v}_{\text{aux}} = 0 \text{ at the interface } z = 0, \quad (\text{III.4c})$$

$$\mathbf{v}_{\text{aux}}(\mathbf{x}) = \mathbf{V}_{\text{aux}}, \quad \text{if } \mathbf{x} \in \mathcal{S}_p, \quad (\text{III.4d})$$

$$\mathbf{v}_{\text{aux}}(|\mathbf{x}| \rightarrow \infty) = 0, \quad (\text{III.4e})$$

$$\overset{\leftrightarrow}{\sigma}_{\text{aux}} := \eta \left[\nabla \mathbf{v}_{\text{aux}} + (\nabla \mathbf{v}_{\text{aux}})^{\dagger} \right] - p_{\text{aux}}\mathcal{I}. \quad (\text{III.4f})$$

The exact solution of these equations for $\mathbf{V} = \mathbf{e}_z\mathcal{V}$ will be provided in Sec. VB. Since both fields $\mathbf{v}(\mathbf{x})$ and $\mathbf{v}_{\text{aux}}(\mathbf{x})$ decay asymptotically at least as $1/x$ for $|\mathbf{x}| \rightarrow \infty$, in Eq. (III.1) the contribution from the surface \mathcal{S}_{∞} vanishes. The remaining terms can be evaluated easily. With Eq. (III.4d) one has

$$\oint_{\mathcal{S}_p} dS \mathbf{n}_{\text{out}} \cdot \overset{\leftrightarrow}{\sigma} \cdot \mathbf{v}_{\text{aux}} = \left(- \oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \overset{\leftrightarrow}{\sigma} \right) \cdot \mathbf{V}_{\text{aux}} = \mathbf{F} \cdot \mathbf{V}_{\text{aux}} \quad (\text{III.5})$$

in terms of the force \mathbf{F} , which the particle exerts on the fluid, and with the unit normal $\mathbf{n} = -\mathbf{n}_{\text{out}}$ oriented into the fluid (as defined in the main text). Similarly, due to Eq. (III.3d) one has

$$\oint_{\mathcal{S}_p} dS \mathbf{n}_{\text{out}} \cdot \overset{\leftrightarrow}{\sigma}_{\text{aux}} \cdot \mathbf{v} = \mathbf{F}_{\text{aux}} \cdot \mathbf{V}. \quad (\text{III.6})$$

Since at the interface the flow \mathbf{v}_{aux} has no vertical component (see Eq. (III.4c)), the application of Eq. (III.3a) gives

$$\int_{\mathcal{D}} d^3\mathbf{x} (\nabla \cdot \vec{\sigma}) \cdot \mathbf{v}_{\text{aux}} = - \int_{z=0} d^2\mathbf{r} \nabla_{\parallel} \gamma(\mathbf{r}) \cdot \mathbf{v}_{\text{aux}}(\mathbf{r}). \quad (\text{III.7})$$

Similarly, Eq. (III.4a) leads to

$$\int_{\mathcal{D}} d^3\mathbf{x} (\nabla \cdot \vec{\sigma}_{\text{aux}}) \cdot \mathbf{v} = 0. \quad (\text{III.8})$$

Inserting these expressions into Eq. (III.1), one finds

$$\mathbf{F}_{\text{aux}} \cdot \boldsymbol{\mathcal{V}} = \mathbf{F} \cdot \boldsymbol{\mathcal{V}}_{\text{aux}} + \int_{z=0} d^2\mathbf{r} \nabla_{\parallel} \gamma(\mathbf{r}) \cdot \mathbf{v}_{\text{aux}}(\mathbf{r}), \quad (\text{III.9})$$

which is the first line of Eq. (4) in the main text.

Turning now to the second line of Eq. (4), we note that the solution $\mathbf{v}_{\text{aux}}(\mathbf{x}')$ can be represented as (see Eq. (34) in Ref. [3])

$$\mathbf{v}_{\text{aux}}(\mathbf{x}') = - \oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \vec{\sigma}_{\text{aux}}(\mathbf{x}) \cdot \mathcal{O}_{\text{aux}}(\mathbf{x}', \mathbf{x}), \quad (\text{III.10})$$

where the non-symmetric, 2nd-rank tensor \mathcal{O}_{aux} is the Green's function of the auxiliary problem, which can be constructed as a superposition of certain singularity solutions and their mirror images with respect to the plane $z = 0$ [4, 5]. In particular, if the point \mathbf{x}' is located at the fluid interface, i.e., $\mathbf{x}' = \mathbf{r}' = (x', y', 0)$, this tensor takes the simple form (see Eq. (25) in Ref. [3])

$$\mathcal{O}_{\text{aux}}(\mathbf{r}', \mathbf{x}) = \mathcal{O}(\mathbf{r}' - \mathbf{x}) \cdot (\mathcal{I} - \mathbf{e}_z \mathbf{e}_z) \quad (\text{III.11})$$

in terms of the (symmetric) Oseen tensor defined in Eq. (5b) in the main text, representing the Green's function for the Stokes equation in an unbounded, homogeneous medium. Therefore, after inserting the integral representation of Eq. (III.10) into Eq. (III.9) and interchanging the integrations, one obtains

$$\begin{aligned} \int_{z=0} d^2\mathbf{r}' \nabla_{\parallel} \gamma(\mathbf{r}') \cdot \mathbf{v}_{\text{aux}}(\mathbf{r}') &= - \oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \vec{\sigma}_{\text{aux}}(\mathbf{x}) \cdot \int_{z=0} d^2\mathbf{r}' \mathcal{O}(\mathbf{r}' - \mathbf{x}) \cdot (\mathcal{I} - \mathbf{e}_z \mathbf{e}_z) \cdot \nabla_{\parallel} \gamma(\mathbf{r}') \\ &= - \oint_{\mathcal{S}_p} dS \mathbf{n} \cdot \vec{\sigma}_{\text{aux}}(\mathbf{x}) \cdot \mathbf{u}(\mathbf{x}) \end{aligned} \quad (\text{III.12})$$

due to $\mathbf{e}_z \cdot \nabla_{\parallel} \gamma = 0$, with the Marangoni flow $\mathbf{u}(\mathbf{x})$ defined in Eq. (5a) in the main text.

In order to obtain Eq. (6) in the main text, we notice that the symmetry of the problem warrants that the translational velocity $\boldsymbol{\mathcal{V}}$ of a force-free ($\mathbf{F} = 0$) moving active particle has only a component in the vertical direction. Therefore, for the application of Eq. (III.9) it suffices to solve the auxiliary problem with a force \mathbf{F}_{aux} acting in the vertical direction. In such a case, $\mathbf{v}_{\text{aux}}(\mathbf{x} = \mathbf{r} + z\mathbf{e}_z)$ is an axisymmetric flow, which can be represented by means of a stream function $\Psi_{\text{aux}}(\mathbf{x}) = \mathcal{V}_{\text{aux}} R^2 \psi_{\text{aux}}(\mathbf{x})$ as [6]

$$\mathbf{v}_{\text{aux}}(\mathbf{x}) = \frac{\mathcal{V}_{\text{aux}} R^2}{r} \left[\frac{\mathbf{r}}{r} \frac{\partial \psi_{\text{aux}}}{\partial z} - \mathbf{e}_z \frac{\partial \psi_{\text{aux}}}{\partial r} \right], \quad (\text{III.13})$$

where $\psi_{\text{aux}}(r = |\mathbf{r}|, z)$ is dimensionless, $\mathcal{V}_{\text{aux}} = \Gamma_z \mathbf{e}_z \cdot \mathbf{F}_{\text{aux}}$, and Γ_z is the L -dependent vertical mobility of a (chemically passive) rigid spherical particle in front of a planar fluid-fluid interface [7] (see the next Sec. concerning the explicit expressions for ψ_{aux} and Γ_z). Thus Eq. (4) in the main text reduces to Eq. (6) after the gradient of the surface tension is replaced by that of the concentration via Eq. (2).

IV. DERIVATION OF EQS. (7) AND (8) IN THE MAIN TEXT

Equations (7) and (8) represent the solution of the differential equations for the Marangoni flow in the asymptotic limit $R/L \rightarrow 0$. First, we consider the boundary-value problem in Eq. (I.5): in this limit, one can approximate the colloidal particle by a point source. Thus Eqs. (I.5a) and (I.5e) can be combined into the single equation

$$\nabla^2 c = - \frac{Q}{D_1} \delta(\mathbf{x} - \mathbf{x}_0), \quad (\text{IV.1})$$

where $\mathbf{x}_0 = (0, 0, L)$ is the position of the center of the particle. The solution of this differential equation, which satisfies the boundary condition in Eq. (I.5b) at infinity, can be constructed via the method of images by making the ansatz

$$c(\mathbf{x}) = c_1^\infty + \frac{1}{4\pi D_1} \left[\frac{Q}{|\mathbf{x} - \mathbf{x}_0|} + \frac{Q'}{|\mathbf{x} - \mathbf{x}_0^*|} \right], \quad z > 0, \quad (\text{IV.2a})$$

$$c(\mathbf{x}) = c_2^\infty + \frac{Q''}{4\pi D_1 |\mathbf{x} - \mathbf{x}_0|}, \quad z < 0, \quad (\text{IV.2b})$$

where $\mathbf{x}_0^* = (0, 0, -L)$ is the mirror point of the center of the particle with respect to the interface; Q' and Q'' represent image sources. (Note that Q'' is defined such that Eq. (IV.2b) contains as a prefactor $1/D_1$ even for $z < 0$.) Their values are determined by the boundary conditions in Eqs. (I.5c) and (I.5d) at the interface, which lead to

$$Q' = \frac{D_1 - \lambda D_2}{2D_+} Q, \quad Q'' = \frac{\lambda D_1}{D_+} Q, \quad D_+ := \frac{1}{2} (D_1 + \lambda D_2). \quad (\text{IV.3})$$

In this manner, Eq. (7) in the main text is derived.

The Marangoni stress associated with the number density profile, given by Eq. (7) in the main text, is

$$\nabla_{\parallel} \gamma(\mathbf{r}) = -b_0 \nabla_{\parallel} [c(\mathbf{r}, z = 0^+) - c_1^\infty] = \frac{Qb_0}{4\pi D_+} \frac{\mathbf{r}}{(r^2 + L^2)^{3/2}}. \quad (\text{IV.4})$$

The Marangoni flow is obtained by evaluating Eq. (5) in the main text. To this end we introduce the Fourier transform of the Oseen tensor [1]

$$\hat{\mathcal{O}}_{\mathbf{k},q} := \int d^2\mathbf{r} dz e^{-i\mathbf{k}\cdot\mathbf{r} - iqz} \mathcal{O}(\mathbf{x} = \mathbf{r} + z\mathbf{e}_z) = \frac{1}{\eta_+(k^2 + q^2)} \left[\mathcal{I} - \frac{(\mathbf{k} + q\mathbf{e}_z)(\mathbf{k} + q\mathbf{e}_z)}{k^2 + q^2} \right], \quad (\text{IV.5a})$$

as well as the Fourier transform of Eq. (IV.4):

$$\int d^2\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla_{\parallel} \gamma(\mathbf{r}) = -i\mathbf{k} \hat{g}_k, \quad (\text{IV.5b})$$

$$\hat{g}_k := b_0 \int d^2\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} [c(\mathbf{r}, z = 0) - c_1^\infty] = \frac{Qb_0}{4\pi D_+} \int d^2\mathbf{r} \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{r^2 + L^2}} = \frac{Qb_0}{2D_+ k} e^{-kL}. \quad (\text{IV.5c})$$

With this, the 2D convolution in Eq. (5a) can be expressed as

$$\begin{aligned} \mathbf{u}(\mathbf{x}) &= \int \frac{d^2\mathbf{k}}{(2\pi)^2} e^{i\mathbf{k}\cdot\mathbf{r}} \hat{g}_k (-i\mathbf{k}) \cdot \int_{-\infty}^{+\infty} \frac{dq}{2\pi} \frac{e^{iqz}}{\eta_+(k^2 + q^2)} \left[\mathcal{I} - \frac{(\mathbf{k} + q\mathbf{e}_z)(\mathbf{k} + q\mathbf{e}_z)}{k^2 + q^2} \right] \\ &= \frac{1}{16\pi^2 \eta_+} \int d^2\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r} - k|z|} \hat{g}_k \frac{(-i\mathbf{k})}{k} \cdot \left[2\mathcal{I} - \frac{\mathbf{k}\mathbf{k}}{k^2} (1 + k|z|) - \mathbf{e}_z \mathbf{e}_z (1 - k|z|) - \left(\frac{\mathbf{k}}{k} \mathbf{e}_z + \mathbf{e}_z \frac{\mathbf{k}}{k} \right) ikz \right] \\ &= \frac{1}{16\pi^2 \eta_+} \int d^2\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r} - k|z|} \hat{g}_k \left[\frac{i\mathbf{k}}{k} (k|z| - 1) - kz\mathbf{e}_z \right] \\ &= \frac{1}{8\pi \eta_+} \int_0^{+\infty} dk k e^{-k|z|} \hat{g}_k \left[\frac{\mathbf{r}}{r} (1 - k|z|) J_1(kr) - \mathbf{e}_z k z J_0(kr) \right], \end{aligned} \quad (\text{IV.6})$$

by computing the integral over q , taking into account that $\mathbf{e}_z \cdot \mathbf{k} = 0$, and exploiting the radial symmetry of the configuration which facilitates the angular integration. With Eq. (IV.5c) for \hat{g}_k , carrying out the last integral in Eq. (IV.6) renders Eq. (8) in the main text.

The Marangoni flow field $\mathbf{u}(\mathbf{x})$ given by Eq. (8) is, as expected, continuous and bounded even at the interface ($z = 0$):

$$\mathbf{u}(\mathbf{r}, z = 0) = \mathbf{e}_r \frac{Qb_0}{16\pi D_+ \eta_+ r} \left[1 - \frac{L(r^2 + L^2)}{[r^2 + L^2]^{3/2}} \right] \sim \begin{cases} \mathbf{e}_r / r, & r \rightarrow \infty, \\ r \mathbf{e}_r, & r \rightarrow 0. \end{cases} \quad (\text{IV.7})$$

For $|\mathbf{x}| = \sqrt{r^2 + z^2} \rightarrow \infty$ Eq. (IV.6) yields the asymptotic behavior $|\mathbf{u}(\mathbf{r}, z)| \propto 1/|\mathbf{x}|$, which, however, *does not* correspond to a hydrodynamic monopole because this asymptotic decay is not spherically symmetric. Instead, $\mathbf{u}(\mathbf{x})$ is the solution of an inhomogeneous Stokes equation with a spatially extended source (see Eq. (III.3a)). The origin of the slow decay $\sim 1/x$ of the field \mathbf{u} can be traced back to the equally slow decay $\sim 1/r$ of the spatially varying surface tension (see Eq. (8) in the main text), so that the capillary forces (in the present case acting as Marangoni stresses) can be balanced by hydrodynamic stresses, as stated by Eq. (3b) in the main text.

V. EXACT SOLUTION FOR THE VELOCITY \mathbf{v}

Since the system under consideration is axisymmetric and involves boundary conditions only at a spherical and at a planar surface, the diffusion and Stokes equations can be solved by employing bipolar coordinates. The bipolar coordinates (ξ, η) , $-\infty < \xi < \infty$, $0 \leq \eta \leq \pi$, are defined¹ such that the vertical coordinate z and the radial distance r from the z -axis are given by [6, 8]

$$z = \varkappa \frac{\sinh \xi}{\cosh \xi - \cos \eta}, \quad r = \varkappa \frac{\sin \eta}{\cosh \xi - \cos \eta}, \quad (\text{V.1})$$

where $\varkappa = R \sinh \xi_0$ and $\xi_0 = \text{arccosh}(L/R)$ are chosen such that the manifold $\xi = \xi_0$ corresponds to the spherical surface of radius R centered at $z = L$ (which is the surface of the particle). The plane $z = 0$ of the interface corresponds to $\xi = 0$. In order to simplify the notation we introduce $\omega := \cos \eta$.

A. Solution of the diffusion equation

The axisymmetric solution to Eq. (1a) can be expressed in terms of the Legendre polynomials P_n as [9]

$$c(\mathbf{x}) = \mathcal{C} + \frac{Q \sinh \xi_0}{4\pi D_1 R} (\cosh \xi - \omega)^{1/2} \sum_{n=0}^{+\infty} \left\{ A_n \sinh \left[\left(n + \frac{1}{2} \right) \xi \right] + B_n \cosh \left[\left(n + \frac{1}{2} \right) \xi \right] \right\} P_n(\omega), \quad \xi > 0, \quad (\text{V.2})$$

in fluid 1, with a similar expression but with different coefficients $\hat{\mathcal{C}}$, \hat{A}_n , and \hat{B}_n in fluid 2 ($\xi < 0$). The prefactor $Q/(D_1 R)$ has the units of a number density, so that the coefficients A_n, B_n, \hat{A}_n , and \hat{B}_n are dimensionless. (We note that the same prefactor $Q/(D_1 R)$ is used for both $\xi > 0$ and $\xi < 0$; see also Eq. (IV.2b).) These coefficients are determined by the boundary conditions expressed in Eqs. (I.5b – I.5e):

1. Since $|\mathbf{x}| \rightarrow \infty$ maps onto $\{\xi = 0, \omega = 1\}$ and because by construction the second term of Eq. (V.2) vanishes in this limit (irrespective of whether $\xi = 0^+$ or $\xi = 0^-$), the boundary condition (I.5b) implies $\mathcal{C} = c_1^\infty$, $\hat{\mathcal{C}} = c_2^\infty$.
2. Since $\xi \rightarrow -\infty$ maps onto $\{r = 0, z = -\varkappa\}$, which is a point within fluid 2, the requirement that the density is bounded everywhere imposes that terms of the form $\exp[-(n + 1/2)\xi]$ cannot occur in the series expansion corresponding to $\xi < 0$. This leads to $\hat{A}_n = \hat{B}_n$. There is no such requirement for $\xi \rightarrow +\infty$, because this maps onto the point $\{r = 0, z = \varkappa\}$ which is located inside the particle.
3. The boundary condition in Eq. (I.5c) concerning the discontinuity of $c(\mathbf{x})$ at the interface ($\xi = 0$) implies (recall that $\hat{\mathcal{C}}/\mathcal{C} = c_2^\infty/c_1^\infty = \lambda$) the relation $\lambda B_n = \hat{B}_n$ ($= \hat{A}_n$, see above).
4. At the interface ($\xi = 0$) one has

$$\left. \frac{\partial c}{\partial z} \right|_{z=0^\pm} = \mathbf{e}_z \cdot \nabla c|_{z=0^\pm} = \frac{1}{h_\xi} \left. \frac{\partial c}{\partial \xi} \right|_{\xi=0^\pm} \quad (\text{V.3})$$

in terms of the corresponding scale factor $h_\xi = \frac{\varkappa}{\cosh \xi - \omega}$. Thus the continuity of the current along the direction of the interface normal (see Eq. (I.5d)) renders the condition

$$\mathbf{e}_z \cdot [D_1 \nabla c|_{z=0^+} - D_2 \nabla c|_{z=0^-}] = 0 \quad \Rightarrow \quad D_1 \left. \frac{\partial c}{\partial \xi} \right|_{\xi=0^+} - D_2 \left. \frac{\partial c}{\partial \xi} \right|_{\xi=0^-} = 0. \quad (\text{V.4})$$

The series representation in Eq. (V.2) gives

$$\left. \frac{\partial c}{\partial \xi} \right|_{\xi=0^+} = \frac{Q \sinh \xi_0}{4\pi D_1 R} (1 - \omega)^{1/2} \sum_{n=0}^{+\infty} \left(n + \frac{1}{2} \right) A_n P_n(\omega), \quad (\text{V.5})$$

¹ We assume that the context suffices to disentangle the same notation η for the bipolar coordinate η and for the viscosity of the fluids.

in fluid 1 ($z \rightarrow 0^+$) and a similar expression with A_n replaced by \hat{A}_n in fluid 2 ($z \rightarrow 0^-$). Therefore, Eq. (V.4) leads to $D_1 A_n = D_2 \hat{A}_n$. Since $\hat{A}_n = \lambda B_n$, it follows that $D_1 A_n = \lambda D_2 B_n$ and Eq. (V.2) turns into

$$c(\mathbf{x}) = c_1^\infty + \frac{Q \sinh \xi_0}{4\pi D_1 R} (\cosh \xi - \omega)^{1/2} \sum_{n=0}^{+\infty} B_n \left\{ \frac{\lambda D_2}{D_1} \sinh \left[\left(n + \frac{1}{2} \right) \xi \right] + \cosh \left[\left(n + \frac{1}{2} \right) \xi \right] \right\} P_n(\omega), \quad \xi > 0, \quad (\text{V.6a})$$

in fluid 1 and, due to $\hat{A}_n = \hat{B}_n = \lambda B_n$ and $c_2^\infty = \lambda c_1^\infty$, into

$$c(\mathbf{x}) = \lambda c_1^\infty + \frac{\lambda Q \sinh \xi_0}{4\pi D_1 R} (\cosh \xi - \omega)^{1/2} \sum_{n=0}^{+\infty} B_n \left\{ \sinh \left[\left(n + \frac{1}{2} \right) \xi \right] + \cosh \left[\left(n + \frac{1}{2} \right) \xi \right] \right\} P_n(\omega), \quad \xi < 0, \quad (\text{V.6b})$$

in fluid 2.

5. The dimensionless coefficients B_n are determined by the boundary condition at the surface of the particle (see Eq. (1b) in the main text). Since at \mathcal{S}_p (i.e., at the surface $\xi = \xi_0$) the normal is $\mathbf{n} = -\mathbf{e}_\xi$, one has

$$\mathbf{n} \cdot \nabla c(\mathbf{x} \in \mathcal{S}_p) = -\frac{1}{h_\xi} \frac{\partial c}{\partial \xi} \Big|_{\xi=\xi_0}. \quad (\text{V.7})$$

Inserting Eq. (V.6a) into Eq. (V.7) and by using the recursion relation

$$(2n+1)\omega P_n(\omega) = (n+1)P_{n+1}(\omega) + nP_{n-1}(\omega), \quad n \geq 0, \quad (\text{V.8})$$

the orthogonality of the Legendre polynomials,

$$\int_{-1}^{+1} ds P_n(s) P_m(s) = \frac{2}{2n+1} \delta_{n,m}, \quad n, m \geq 0, \quad (\text{V.9})$$

and the following expressions for the integral [9]

$$\int_{-1}^{+1} d\omega \frac{P_n(\omega)}{(\cosh \xi_0 - \omega)^{1/2}} = \frac{2\sqrt{2}}{2n+1} e^{-(n+1/2)\xi_0}, \quad \xi_0 > 0, \quad (\text{V.10})$$

one can transform the boundary condition in Eq. (1b) into a set of linear equations for the coefficients B_n :

$$\begin{aligned} 2\sqrt{2} e^{-(n+1/2)\xi_0} = (n+1)(B_n - B_{n+1}) & \left\{ \frac{\lambda D_2}{D_1} \cosh \left[\left(n + \frac{3}{2} \right) \xi \right] + \sinh \left[\left(n + \frac{3}{2} \right) \xi \right] \right\} \\ & + n(B_n - B_{n-1}) \left\{ \frac{\lambda D_2}{D_1} \cosh \left[\left(n - \frac{1}{2} \right) \xi \right] + \sinh \left[\left(n - \frac{1}{2} \right) \xi \right] \right\}, \quad n \geq 0, \quad (\text{V.11}) \end{aligned}$$

with the convention that $B_{-1} = 0$.

This infinitely large system of linear equations is truncated at a sufficiently large index $n = N$ and it is then solved numerically. In practice, the truncation, as well as the series representation, are converging very fast. We have found that $N = 50$ is sufficient for providing accurate results. As an illustrative example of a calculation following the steps outlined above, in Fig. S1 we show plots of the field $c(\mathbf{x})$.

B. Solution of the auxiliary problem in terms of bipolar coordinates

Our auxiliary problem of a (passive) sphere approaching a flat and not deforming fluid-fluid interface (Eq. (III.4)) has been solved previously in terms of bipolar coordinates by Bart [10] and by Lee and Leal [7]. Nevertheless, we provide here the details of the solution for the auxiliary problem because the former reference [10] provides only the sum of the coefficients in the series representation of the solution (see below), which is insufficient for our problem (see, c.f., Eq. (V.41)), while the latter reference [7] provides expressions for these coefficients (Eqs. (61)–(66) in Ref. [7]) which, however, in certain limits do not reduce to those corresponding to the limiting cases of a solid-liquid interface

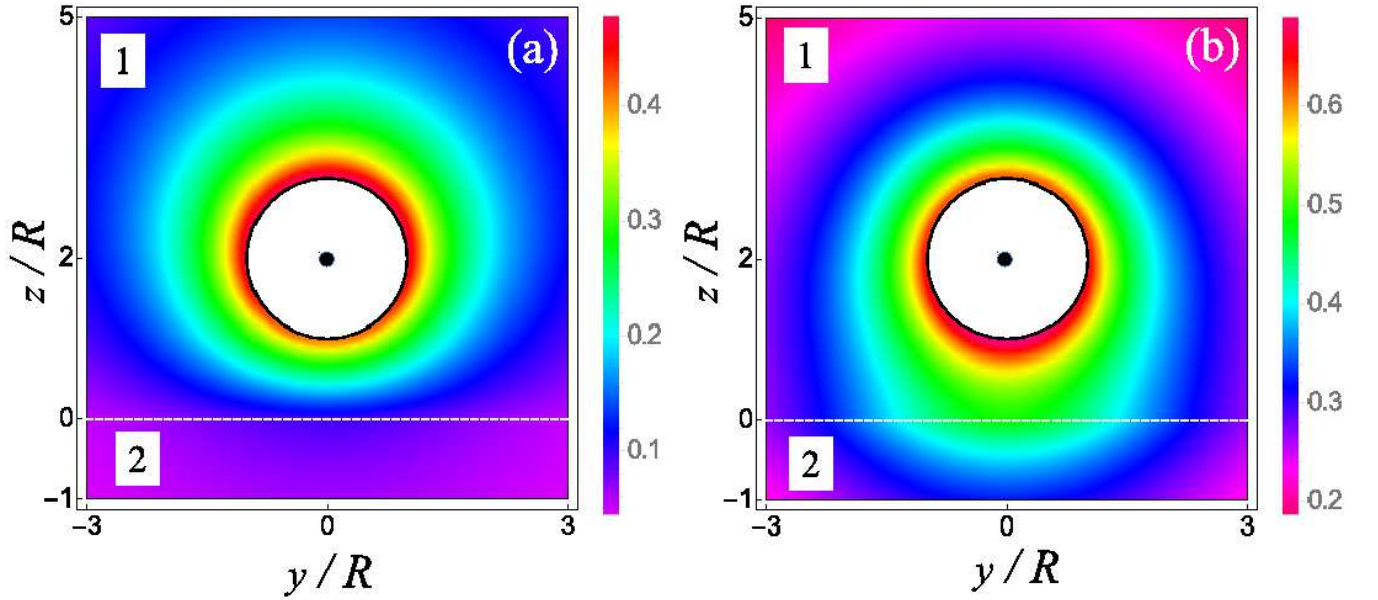


FIG. S1. Plots of the number density $c(\mathbf{x}) - c_1^\infty$ (in units of $Q \sinh \xi_0 / (4\pi D_1 R)$, see Eq. (V.6a)) in the y - z plane for a spherical particle located at $z/R = L/R = 2$ for $\lambda = 1$ (i.e., $c_2^\infty = c_1^\infty$) and (a) $D_2/D_1 = 5$ and (b) $D_2/D_1 = 1/5$, respectively. Note that, for reasons of clarity concerning the details close to the interface $z = 0$, the color coding scales in (a) and (b) are different. The whole surface of the particle is chemically active and homogeneous.

($\eta_2/\eta_1 \rightarrow \infty$) or of a “free”, i.e., liquid–gas interface ($\eta_2/\eta_1 \rightarrow 0$) as derived by Brenner [8]². The axial symmetry of the problem allows one to express the solution of the Stokes equations in terms of a dimensionless stream function $\psi_{\text{aux}}(\mathbf{x})$ (see Eq. (III.13)), which can be represented in bipolar coordinates [8, 9]:

$$\psi_{\text{aux}}(\mathbf{x}) = \frac{1}{(\cosh \xi - \omega)^{3/2}} \sum_{n=1}^{+\infty} \left\{ K_n \cosh \left[\left(n - \frac{1}{2} \right) \xi \right] + L_n \sinh \left[\left(n - \frac{1}{2} \right) \xi \right] \right. \\ \left. + M_n \cosh \left[\left(n + \frac{3}{2} \right) \xi \right] + N_n \sinh \left[\left(n + \frac{3}{2} \right) \xi \right] \right\} \times \mathcal{G}_{n+1}^{-1/2}(\omega), \quad \xi > 0; \quad (\text{V.12})$$

a similar expression, but with different coefficients \hat{K}_n , \hat{L}_n , \hat{M}_n , and \hat{N}_n , holds for $\xi < 0$, where

$$\mathcal{G}_n^{-1/2}(\omega) = \frac{P_{n-2}(\omega) - P_n(\omega)}{2n - 1} \quad (\text{V.13})$$

denotes the Gegenbauer polynomial of order n and degree $-1/2$ [8]. The dimensionless coefficients K_n , L_n , M_n , and N_n , as well as the hatted ones, depend on ξ_0 and are determined by the boundary conditions for the velocity field (see Eq. (III.4)). We proceed along the lines of the previous section for determining the stream function:

1. The stream function given by Eq. (V.12) automatically satisfies the boundary condition of vanishing velocity at infinity [6].
2. Boundedness of the fields everywhere in the fluid domain, in particular at the point $\xi \rightarrow -\infty$ located in fluid 2, imposes that none of the terms $\sim \exp[-(n - 1/2)\xi]$ and $\sim \exp[-(n + 3/2)\xi]$ is present in the series expansion corresponding to $\xi < 0$. This leads to

$$\hat{K}_n = \hat{L}_n, \quad \hat{M}_n = \hat{N}_n, \quad n \geq 1. \quad (\text{V.14})$$

² For example, in both limits Eqs. (64)–(66) in Ref. [7] lead to expressions which differ by a factor of $1/(2n + 1)$ within the sums from the corresponding Eqs. (2.19) and (3.13) in Ref. [8]. However, the results for the so-called Stokes’ law correction shown in Fig. 2 in Ref. [7] seem to be in agreement with the behavior expected from Ref. [8]. We therefore surmise that (some of) the expressions in Eqs. (61)–(66) in Ref. [7] contain errors, which are of typographical nature (only).

3. Due to Eq. (III.13), the requirement that the normal velocity vanishes at the interface in both fluid domains translates into

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial r} \right|_{z=0^\pm} = 0. \quad (\text{V.15})$$

Since the interface ($z = 0$) coincides with the surface $\xi = 0$, this means (see also Eq. (3.3) in Ref. [8])

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial \omega} \right|_{\xi=0^\pm} = 0. \quad (\text{V.16})$$

This leads to

$$K_n = -M_n, \quad \hat{K}_n = -\hat{M}_n, \quad n \geq 1, \quad (\text{V.17})$$

which implies necessarily the continuity of ψ_{aux} at the interface: $\psi_{\text{aux}}(\xi = 0^+, \omega) = \psi_{\text{aux}}(\xi = 0^-, \omega) = 0$. The last relation together with Eq. (V.14) implies

$$\hat{K}_n = \hat{L}_n = -\hat{M}_n = -\hat{N}_n, \quad n \geq 1. \quad (\text{V.18})$$

4. Due to Eq. (III.13) and to an argument as the one used in Eq. (V.3) (see also Eq. (8) in Ref. [10]), continuity of the tangential velocity at the interface translates into

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0^+} - \left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0^-} = 0 \quad \Rightarrow \quad \left. \frac{\partial \psi_{\text{aux}}}{\partial \xi} \right|_{\xi=0^+} - \left. \frac{\partial \psi_{\text{aux}}}{\partial \xi} \right|_{\xi=0^-} = 0, \quad (\text{V.19})$$

from which one obtains

$$\left(n - \frac{1}{2}\right) L_n + \left(n + \frac{3}{2}\right) N_n = \left(n - \frac{1}{2}\right) \hat{L}_n + \left(n + \frac{3}{2}\right) \hat{N}_n, \quad n \geq 1. \quad (\text{V.20})$$

Together with Eq. (V.18), this leads to

$$\hat{K}_n = -\frac{1}{2} \left[\left(n - \frac{1}{2}\right) L_n + \left(n + \frac{3}{2}\right) N_n \right], \quad n \geq 1. \quad (\text{V.21})$$

5. The last one of the boundary conditions at the interface is the continuity of the tangential stresses. (We remind the reader that the auxiliary problem involves an *inert* (*i.e.*, *non-active*) particle. In this case there are no lateral variations of the surface tension of the interface. Therefore in the auxiliary problem there is no Maragoni stress induced, and thus Eq. (3b) implies continuity of the tangential stresses.) Using Eq. (III.13) and the vanishing of the normal velocity at the interface reduces Eq. (3b) in the main text to (see also Eqs. (3.1)–(3.4) in Ref. [8] for expressing the stress tensor components in terms of the stream function)

$$\eta_1 \left. \frac{\partial^2 \psi_{\text{aux}}}{\partial z^2} \right|_{z=0^+} - \eta_2 \left. \frac{\partial^2 \psi_{\text{aux}}}{\partial z^2} \right|_{z=0^-} = 0 \quad \Rightarrow \quad \eta_1 \left. \frac{\partial^2 \psi_{\text{aux}}}{\partial \xi^2} \right|_{\xi=0^+} - \eta_2 \left. \frac{\partial^2 \psi_{\text{aux}}}{\partial \xi^2} \right|_{\xi=0^-} = 0. \quad (\text{V.22})$$

The latter equation follows from iterating an argument as the one given in Eq. (V.3) (see also Eqs. (3.1)–(3.4) in Ref. [8]). By taking advantage of the continuity of ψ_{aux} at $\xi = 0$, which facilitates the simplification of the expressions for the second derivatives evaluated at the interface³, one arrives at

$$\eta_1 \left[\left(n - \frac{1}{2}\right)^2 K_n + \left(n + \frac{3}{2}\right)^2 M_n \right] = \eta_2 \left[\left(n - \frac{1}{2}\right)^2 \hat{K}_n + \left(n + \frac{3}{2}\right)^2 \hat{M}_n \right]. \quad (\text{V.23})$$

By combining Eq. (V.23) with Eqs. (V.17) and (V.21) one obtains

$$K_n = \frac{\eta_2}{\eta_1} \hat{K}_n = -\frac{\eta_2}{2\eta_1} \left[\left(n - \frac{1}{2}\right) L_n + \left(n + \frac{3}{2}\right) N_n \right], \quad n \geq 1. \quad (\text{V.24})$$

³ With the notations (the prime denotes the derivative with respect to ξ) $f(\xi, \omega) = (\cosh \xi - \omega)^{-3/2}$, $g(\xi, \omega) = f'(\xi, \omega)/f(\xi, \omega)$, and $\Phi(\xi, \omega) = \psi_{\text{aux}}(\xi, \omega)/f(\xi, \omega)$, one has $\psi_{\text{aux}}'' = g' \psi_{\text{aux}} + g(\psi_{\text{aux}}' + f\Phi') + f\Phi''$. Noting that at the interface ($\xi = 0$) both g and ψ_{aux} vanish (the latter due to point 3 above), while f is continuous across the interface, one infers that the jump of ψ_{aux}'' at the interface implies that at the interface Φ'' exhibits a jump ψ_{aux}''/f , from which Eq. (V.23) follows.

6. Turning now to the boundary conditions at the sphere, the no-slip requirement (Eq. (III.3d)) implies that at \mathcal{S}_p \mathbf{v}_{aux} has only a z component, which is equal to \mathcal{V}_{aux} . Using the representation of \mathbf{v}_{aux} in terms of the stream function (Eq. (III.13)) one obtains

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{\mathbf{x} \in \mathcal{S}_p} = 0, \quad -\frac{R^2}{r} \left. \frac{\partial \psi_{\text{aux}}}{\partial r} \right|_{\mathbf{x} \in \mathcal{S}_p} = 1. \quad (\text{V.25})$$

Using Eq. (V.25) and the chain rule for computing nested derivatives (see also Eqs. (2.3) and (2.4) in Ref. [8]), one obtains the following equivalent conditions (the surface of the particle is given by $\xi = \xi_0$):

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial \omega} \right|_{\xi=\xi_0} = -\frac{\partial}{\partial \omega} \left(\frac{r^2}{2R^2} \right)_{\xi=\xi_0}, \quad \left. \frac{\partial \psi_{\text{aux}}}{\partial \xi} \right|_{\xi=\xi_0} = -\frac{\partial}{\partial \xi} \left(\frac{r^2}{2R^2} \right)_{\xi=\xi_0}. \quad (\text{V.26})$$

The first of these two equations can be integrated over ω . Since $\omega = +1$ implies $r = 0$ (see Eq. (V.1)) and $\psi_{\text{aux}}(\xi_0, \omega = +1) = 0$ (see Eq. (V.12) with $\mathcal{G}_{n+1}^{-1/2}(1) = 0$), one finds [8]

$$\psi_{\text{aux}}(\xi, \omega)|_{\xi=\xi_0} = -\frac{r^2}{2R^2} \Big|_{\xi=\xi_0} \Rightarrow (\cosh \xi - \omega)^{3/2} \psi_{\text{aux}}(\xi, \omega) \Big|_{\xi=\xi_0} = -(\cosh \xi - \omega)^{3/2} \frac{r^2}{2R^2} \Big|_{\xi=\xi_0}. \quad (\text{V.27a})$$

The second equation in Eq. (V.26) can be cast into the form

$$\frac{\partial}{\partial \xi} \left[(\cosh \xi - \omega)^{3/2} \psi_{\text{aux}}(\xi, \omega) \right] \Big|_{\xi=\xi_0} = -\frac{\partial}{\partial \xi} \left[(\cosh \xi - \omega)^{3/2} \frac{r^2}{2R^2} \right] \Big|_{\xi=\xi_0}. \quad (\text{V.27b})$$

This can be checked by differentiating the products on each side and by using Eq. (V.27a). By using the expansion (with $\varkappa = R \sinh \xi_0$ and $r = \varkappa \sqrt{1 - \omega^2} / (\cosh \xi - \omega)$) [8]

$$(\cosh \xi - \omega)^{3/2} r^2 = \sqrt{2} \varkappa^2 \sum_{n=1}^{\infty} n(n+1) \left[\frac{e^{-(n-1/2)\xi}}{2n-1} - \frac{e^{-(n+3/2)\xi}}{2n+3} \right] \times \mathcal{G}_{n+1}^{-1/2}(\omega) \quad (\text{V.28})$$

and by employing the orthogonality of the Gegenbauer polynomials $\{\mathcal{G}_n^{-1/2}\}_{n \geq 2}$ one can transform Eq. (V.27) into equalities of individual terms:

$$\begin{aligned} K_n \cosh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] + L_n \sinh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] + M_n \cosh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] + N_n \sinh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] \\ = -\frac{\sqrt{2}}{4} (\sinh \xi_0)^2 n(n+1) \left[\frac{e^{-(n-1/2)\xi_0}}{n-1/2} - \frac{e^{-(n+3/2)\xi_0}}{n+3/2} \right], \quad n \geq 1, \end{aligned} \quad (\text{V.29a})$$

and

$$\begin{aligned} \left(n - \frac{1}{2} \right) \left\{ K_n \sinh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] + L_n \cosh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] \right\} \\ + \left(n + \frac{3}{2} \right) \left\{ M_n \sinh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] + N_n \cosh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] \right\} \\ = -\frac{\sqrt{2}}{4} (\sinh \xi_0)^2 n(n+1) \left[-e^{-(n-1/2)\xi_0} + e^{-(n+3/2)\xi_0} \right], \quad n \geq 1. \end{aligned} \quad (\text{V.29b})$$

By using Eqs. (V.17) and (V.24) in order to replace K_n and M_n in Eq. (V.29), for every $n \geq 1$ one obtains a system of linear equations with the unknowns L_n and N_n , the solution of which is

$$L_n = -\frac{\sqrt{2}}{4} (\sinh \xi_0)^2 n(n+1) \frac{\chi_n^{(1)} \beta_n^{(2)} - \chi_n^{(2)} \beta_n^{(1)}}{\alpha_n^{(1)} \beta_n^{(2)} - \alpha_n^{(2)} \beta_n^{(1)}}, \quad (\text{V.30a})$$

$$N_n = -\frac{\sqrt{2}}{4} (\sinh \xi_0)^2 n(n+1) \frac{\chi_n^{(2)} \alpha_n^{(1)} - \chi_n^{(1)} \alpha_n^{(2)}}{\alpha_n^{(1)} \beta_n^{(2)} - \alpha_n^{(2)} \beta_n^{(1)}}, \quad (\text{V.30b})$$

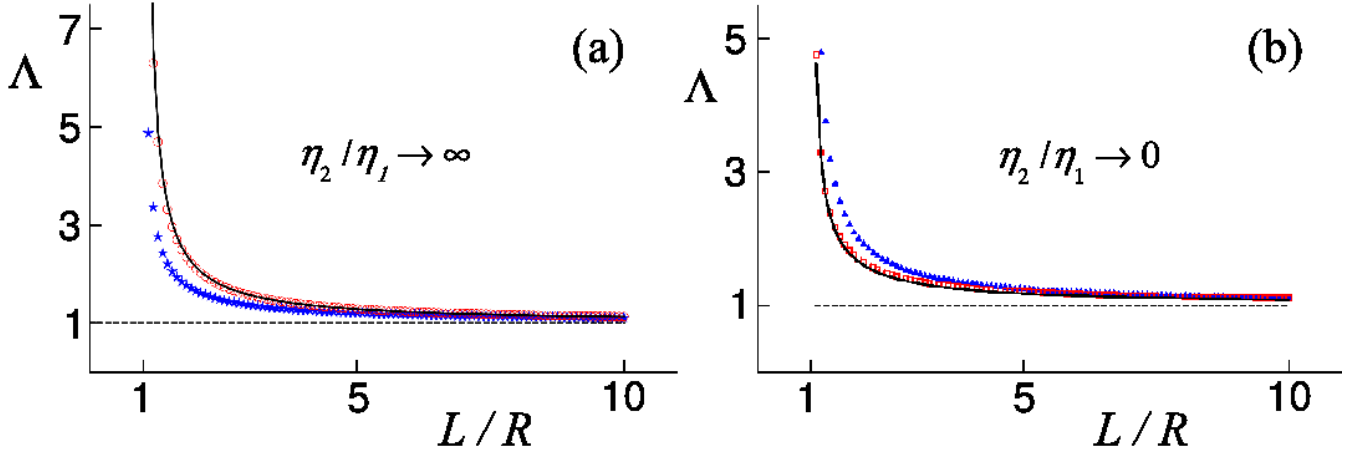


FIG. S2. The “Stokes’ law correction” $\Lambda(L/R; \eta_2/\eta_1)$ (Eq. (V.32)) as a function of L/R for (a) $\eta_2/\eta_1 = 0.1(\star)$, $20(\circ)$ and (b) $\eta_2/\eta_1 = 2(\blacktriangle)$, $0.05(\square)$, respectively. The plots illustrate the convergence of $\Lambda(L/R; \eta_2/\eta_1)$ in the limits $\eta_2/\eta_1 \rightarrow \infty$ (a) and $\eta_2/\eta_1 \rightarrow 0$ (b), respectively, towards the limiting curves (solid lines) corresponding to (a) a particle approaching a solid wall (Eq. (2.19) in Ref. [8]) and (b) a particle approaching a “free” (liquid–gas) interface (Eq. (3.13) in Ref. [8]). The dashed lines show the expected asymptotic behavior $\Lambda(L/R \rightarrow \infty; \eta_2/\eta_1) = 1$.

where

$$\begin{aligned}
 \chi_n^{(1)} &= \frac{e^{-(n-1/2)\xi_0}}{n-1/2} - \frac{e^{-(n+3/2)\xi_0}}{n+3/2}, \\
 \chi_n^{(2)} &= -e^{-(n-1/2)\xi_0} + e^{-(n+3/2)\xi_0}, \\
 \alpha_n^{(1)} &= \sinh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] + \frac{\eta_2}{2\eta_1} \left(n - \frac{1}{2} \right) \left\{ \cosh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] - \cosh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] \right\}, \\
 \beta_n^{(1)} &= \sinh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] + \frac{\eta_2}{2\eta_1} \left(n + \frac{3}{2} \right) \left\{ \cosh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] - \cosh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] \right\}, \\
 \alpha_n^{(2)} &= \left(n - \frac{1}{2} \right) \left\{ \cosh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] + \frac{\eta_2}{2\eta_1} \left\{ \left(n + \frac{3}{2} \right) \sinh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] - \left(n - \frac{1}{2} \right) \sinh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] \right\} \right\}, \\
 \beta_n^{(2)} &= \left(n + \frac{3}{2} \right) \left\{ \cosh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] + \frac{\eta_2}{2\eta_1} \left\{ \left(n + \frac{3}{2} \right) \sinh \left[\left(n + \frac{3}{2} \right) \xi_0 \right] - \left(n - \frac{1}{2} \right) \sinh \left[\left(n - \frac{1}{2} \right) \xi_0 \right] \right\} \right\}.
 \end{aligned} \tag{V.31}$$

The coefficients K_n and, due to Eq. (V.17), $M_n = -K_n$ and \hat{K}_n are determined by Eqs. (V.24) and (V.21). The other hatted coefficients follow from Eqs. (V.18), (V.23), and (V.24). This concludes the derivation.

Once the coefficients K_n, M_n, L_n , and N_n are known, one can determine the force \mathbf{F}_{aux} exerted by the particle on the fluid (compare Eq. (III.6)) from the stream function $\Psi_{\text{aux}} = \mathcal{V}_{\text{aux}} R^2 \psi_{\text{aux}}(\mathbf{x})$ as [7–10]:

$$\begin{aligned}
 \mathbf{F}_{\text{aux}} &= -\mathbf{e}_z \frac{2\sqrt{2}\pi\eta_1}{\kappa} \mathcal{V}_{\text{aux}} R^2 \sum_{n=1}^{\infty} (K_n + L_n + M_n + N_n) = -\mathbf{e}_z \frac{2\sqrt{2}\pi}{\sinh \xi_0} \eta_1 R \mathcal{V}_{\text{aux}} \sum_{n=1}^{\infty} (L_n + N_n) \\
 &=: \mathbf{e}_z (6\pi\eta_1 R \mathcal{V}_{\text{aux}}) \Lambda(L/R; \eta_2/\eta_1).
 \end{aligned} \tag{V.32}$$

In the limits $\eta_2/\eta_1 \rightarrow \infty$ and $\eta_2/\eta_1 \rightarrow 0$, the so-called [8] “Stokes’ law correction” $\Lambda(L/R; \eta_2/\eta_1)$ should recover the exact results obtained by Brenner (Eqs. (2.19) and (3.13) in Ref. [8]) for the case of a particle approaching a hard wall (i.e., $\eta_2 \rightarrow \infty$) and a “free” (liquid–gas) interface (i.e., $\eta_2 = 0$), respectively. As shown in Fig. S2, $\Lambda(L/R; \eta_2/\eta_1)$ indeed exhibits this expected behavior, which provides a welcome check of our derivation.

C. Calculation of the drift velocity \mathbf{V} in terms of bipolar coordinates

In this subsection we evaluate Eq. (6) in the main text with the expressions derived for the fields $c(\mathbf{x})$ and $\psi_{\text{aux}}(\mathbf{x})$. Since the interface ($z = 0$) coincides with the surface $\xi = 0$, in the integral in Eq. (6) one has

$$dr \left. \frac{\partial c}{\partial r} \right|_{z=0+} = d\omega \left. \frac{\partial c}{\partial \omega} \right|_{\xi=0+}. \quad (\text{V.33})$$

Therefore, from Eq. (V.6a) one finds

$$dr \left. \frac{\partial c}{\partial r} \right|_{z=0+} = \frac{d\omega}{\sqrt{1-\omega}} \frac{Q \sinh \xi_0}{4\pi D_1 R} \sum_{n=0}^{\infty} B_n \left[(1-\omega) \frac{dP_n}{d\omega} - \frac{1}{2} P_n(\omega) \right]. \quad (\text{V.34})$$

Equation (V.12) leads to (see also Eqs. (V.3) and (V.19))

$$\left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0} = \frac{1}{\varkappa \sqrt{1-\omega}} \sum_{n=1}^{\infty} \left[\left(n - \frac{1}{2} \right) L_n + \left(n + \frac{3}{2} \right) N_n \right] \times \mathcal{G}_{n+1}^{-1/2}(\omega), \quad (\text{V.35})$$

so that the integral in Eq. (6) turns into

$$\begin{aligned} \int_0^{\infty} dr \left. \frac{\partial c}{\partial r} \right|_{z=0+} \left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0} &= \frac{Q}{4\pi D_1 R^2} \sum_{n=1}^{\infty} \frac{1}{2n+1} \left[\left(n - \frac{1}{2} \right) L_n + \left(n + \frac{3}{2} \right) N_n \right] \sum_{m=0}^{\infty} B_m \\ &\times \int_{-1}^{+1} d\omega \frac{1}{1-\omega} [P_{n-1}(\omega) - P_{n+1}(\omega)] \left[(1-\omega) \frac{dP_m}{d\omega} - \frac{1}{2} P_m(\omega) \right], \end{aligned} \quad (\text{V.36})$$

with B_m given by Eq. (V.11). From the identities (see Subsect. VD)

$$\int_{-1}^{+1} d\omega [P_{n-1}(\omega) - P_{n+1}(\omega)] \frac{dP_m}{d\omega} = 2\delta_{n,m} (1 - \delta_{m,0}), \quad (\text{V.37a})$$

and

$$\frac{1}{2} \int_{-1}^{+1} d\omega \frac{1}{1-\omega} [P_{n-1}(\omega) - P_{n+1}(\omega)] P_m(\omega) = \begin{cases} (2n+1)/[n(n+1)], & m < n, \\ 1/(n+1), & m = n, \\ 0, & n < m, \end{cases} \quad (\text{V.37b})$$

which are valid for $n \geq 1$ and $m \geq 0$, one obtains for the sum over m the simple expression

$$\sum_{m=0}^{\infty} B_m \times \int_{-1}^{+1} d\omega \frac{1}{1-\omega} [P_{n-1}(\omega) - P_{n+1}(\omega)] \left[(1-\omega) \frac{dP_m}{d\omega} - \frac{1}{2} P_m(\omega) \right] = \frac{2n+1}{n+1} \left[B_n - \frac{1}{n} \sum_{m=0}^{n-1} B_m \right], \quad (\text{V.38})$$

and thus finally arrives at

$$\int_0^{\infty} dr \left. \frac{\partial c}{\partial r} \right|_{z=0+} \left. \frac{\partial \psi_{\text{aux}}}{\partial z} \right|_{z=0} = \frac{Q}{4\pi D_1 R^2} \sum_{n=1}^{\infty} \frac{1}{n+1} \left[\left(n - \frac{1}{2} \right) L_n + \left(n + \frac{3}{2} \right) N_n \right] \left[B_n - \frac{1}{n} \sum_{m=0}^{n-1} B_m \right]. \quad (\text{V.39})$$

The force \mathbf{F}_{aux} needed to drag the particle with velocity $\mathbf{e}_z \mathcal{V}_{\text{aux}}$ is given by Eq. (V.32). Thus, the mobility Γ_z for the auxiliary problem (see the text below Eq. (III.13)) is given by

$$\Gamma_z := \frac{\mathcal{V}_{\text{aux}}}{\mathbf{e}_z \cdot \mathbf{F}_{\text{aux}}} = -\frac{\sinh \xi_0}{2\sqrt{2}\pi\eta_1 R} \left[\sum_{n=1}^{\infty} (L_n + N_n) \right]^{-1}. \quad (\text{V.40})$$

Therefore, the expression for the velocity \mathbf{V} given by Eq. (6) and normalized by $u(\mathbf{x}_0 = (0, 0, L))$ (see Eqs. (8) and (9) in the main text) can be written (using $\cosh \xi_0 = L/R$) as

$$\begin{aligned} \frac{\mathbf{V} \cdot \mathbf{e}_z}{\mathbf{u}(\mathbf{x}_0) \cdot \mathbf{e}_z} &= -\sqrt{2} \left(1 + \frac{\lambda D_2}{D_1} \right) \left(1 + \frac{\eta_2}{\eta_1} \right) \sinh(2\xi_0) \left[\sum_{n=1}^{\infty} (L_n + N_n) \right]^{-1} \\ &\times \sum_{n=1}^{\infty} \frac{1}{n+1} \left[\left(n - \frac{1}{2} \right) L_n + \left(n + \frac{3}{2} \right) N_n \right] \left[B_n - \frac{1}{n} \sum_{m=0}^{n-1} B_m \right], \end{aligned} \quad (\text{V.41})$$

which is the function plotted in Fig. 3 of the main text.

D. Derivation of Eq. (V.37)

We note that due to $P_0 = 1$ the integral on the left hand side (lhs) of Eq. (V.37a) is zero for $m = 0$. For $m \neq 0$ we employ the relation

$$\frac{d}{d\omega} [P_{n+1}(\omega) - P_{n-1}(\omega)] = (2n+1)P_n(\omega), \quad (\text{V.42})$$

which can be obtained by straightforward differentiation of the defining expression for the Legendre polynomials (Rodriguez formula). This allows one to transform the lhs of Eq. (V.37a) as follows:

$$\begin{aligned} \int_{-1}^{+1} d\omega [P_{n-1}(\omega) - P_{n+1}(\omega)] \frac{dP_m}{d\omega} &= \{P_m(\omega) [P_{n-1}(\omega) - P_{n+1}(\omega)]\}_{\omega=-1}^{\omega=+1} - \int_{-1}^{+1} d\omega P_m(\omega) \frac{d}{d\omega} [P_{n-1}(\omega) - P_{n+1}(\omega)] \\ &= (2n+1) \int_{-1}^{+1} d\omega P_m(\omega) P_n(\omega) = 2\delta_{n,m}, \end{aligned} \quad (\text{V.43})$$

where in the first line the first term on the rhs vanishes due to $P_n(1) = 1$, $P_n(-1) = (-1)^n$, $n \geq 0$, and the last equality follows from the orthogonality of the Legendre polynomials (Eq. (V.9)). Combining the results for $m = 0$ and $m \neq 0$ by accounting for the vanishing of the integral for $m = 0$ via the factor $(1 - \delta_{m,0})$ completes the derivation of Eq. (V.37a).

The identity

$$P_{n-1}(\omega) - P_{n+1}(\omega) = \frac{2n+1}{n(n+1)}(1-\omega^2)\frac{dP_n}{d\omega}, \quad n \geq 1, \quad (\text{V.44})$$

follows from the recursion relations for the Legendre polynomials. Therefore, the integral $I_{m,n}$ in Eq. (V.37b) can be written as

$$I_{m,n} := \frac{2n+1}{2n(n+1)} \int_{-1}^{+1} d\omega (1+\omega) P_m(\omega) \frac{dP_n}{d\omega}, \quad m \geq 0, n \geq 1. \quad (\text{V.45})$$

One also has the identities (summation theorems [11]):

$$\frac{dP_n}{d\omega} = 2 \sum_{k=0}^{[(n-1)/2]} \left(n - 2k - \frac{1}{2}\right) P_{n-2k-1}(\omega), \quad n \geq 1, \quad (\text{V.46a})$$

and

$$\omega \frac{dP_n}{d\omega} = nP_n(\omega) + 2(1 - \delta_{n,1}) \sum_{k=0}^{[(n-2)/2]} \left(n - 2k - \frac{3}{2}\right) P_{n-2k-2}(\omega), \quad n \geq 1, \quad (\text{V.46b})$$

where $[\dots]$ denotes the integer part of the quantity in square brackets. Inserting these expressions into Eq. (V.45) and using the orthogonality relations in Eq. (V.9) one finds

$$I_{m,n} = \frac{2n+1}{n(n+1)} \left[\frac{n}{2n+1} \delta_{n,m} + \sum_{k=0}^{[(n-1)/2]} \delta_{m,n-2k-1} + (1 - \delta_{n,1}) \sum_{k=0}^{[(n-2)/2]} \delta_{m,n-2k-2} \right], \quad m \geq 0, n \geq 1. \quad (\text{V.47})$$

In the sums, the corresponding indices take the values

$$\sum_{k=0}^{[(n-1)/2]} \delta_{m,n-2k-1} = \begin{cases} \delta_{m,n-1} + \delta_{m,n-3} + \dots + \delta_{m,0}, & n \text{ odd}, \\ \delta_{m,n-1} + \delta_{m,n-3} + \dots + \delta_{m,1}, & n \text{ even}, \end{cases} \quad (\text{V.48a})$$

and

$$\sum_{k=0}^{[(n-2)/2]} \delta_{m,n-2k-2} = \begin{cases} \delta_{m,n-2} + \delta_{m,n-4} + \dots + \delta_{m,1}, & n \text{ odd}, \\ \delta_{m,n-2} + \delta_{m,n-4} + \dots + \delta_{m,0}, & n \text{ even}, \end{cases} \quad (\text{V.48b})$$

so that Eq. (V.47) can be written as

$$I_{m,n} = \frac{2n+1}{n(n+1)} \left[\frac{n}{2n+1} \delta_{n,m} + \sum_{j=0}^{n-1} \delta_{m,j} \right], \quad m \geq 0, n \geq 1, \quad (\text{V.49})$$

which leads to Eq. (V.37b).

VI. PARTICLE DRIFT INDUCED BY MARANGONI FLOW

In this section we estimate the particle drift due to the Marangoni flow generated by the chemical activity of the particle. In the limit $R/L \rightarrow 0$ one can use Eq. (9) in order to integrate the equation of motion

$$\frac{dL}{dt} = \mathbf{e}_z \cdot \mathbf{v} \approx -\frac{Qb_0}{64\pi D_+ \eta_+ L} \quad (\text{VI.1})$$

within the overdamped regime of the dynamics. Consistently with the physical assumptions of the underlying model, this expression implies an “adiabatic approximation”: the particle drift is sufficiently slow so that both the number density field $c(\mathbf{x})$ and the Marangoni flow can be computed as stationary solutions of the diffusion equation or of the Stokes equations, respectively. The solution of Eq. (VI.1) with the arbitrary initial condition $L(0) = L_0$ is

$$L^2(t) = L_0^2 - \frac{Qb_0}{32\pi D_+ \eta_+} t. \quad (\text{VI.2})$$

Consider for simplicity the case $b_0 > 0$, $Q > 0$, so that the particle drifts towards the interface. We introduce the time t_{drift} by the condition $L(t_{\text{drift}}) = R$, i.e., after t_{drift} the particle touches the interface. If initially $L_0 \gg R$, the explicit solution above leads to

$$t_{\text{drift}} = \frac{32\pi D_+ \eta_+ L_0^2}{Qb_0}. \quad (\text{VI.3})$$

When compared with the diffusion time for the particle over the same distance,

$$t_{\text{diff}} = \frac{L_0^2}{D_p} = \frac{6\pi\eta_+ R L_0^2}{k_B T}, \quad (\text{VI.4})$$

with the coefficient of diffusion of the colloidal particle D_p as quoted in the main text, one obtains the ratio

$$\frac{t_{\text{drift}}}{t_{\text{diff}}} = \frac{1}{2q} \quad (\text{VI.5})$$

in terms of the dimensionless parameter q introduced in Eq. (10) in the main text. We point out that in the limit $L_0 \gg R$ the drift time t_{drift} is independent of the specific value of the final separation $L(t_{\text{drift}}) = R$. In particular, one could have as well set $R \rightarrow 0$ from the beginning so that $L \gg R$ is always fulfilled. This indicates that, during the drift, the particle spends most of the time in the spatial region where $L \gg R$, i.e., where the approximation for \mathbf{v} , described by Eq. (9) in the main text, is reliable. This provides a successful self-consistency check of the point-particle approximation employed in Eq. (VI.1). Finally, in the opposite case ($Q < 0$) that the particle drifts away from the interface, t_{drift} has to be interpreted as the time for the particle to reach a distance $\hat{L} \gg R$ with the initial condition $L(0) = R$, i.e., $\hat{L}^2 = R^2 - Qb_0 t_{\text{drift}} / (32\pi D_+ \eta_+)$. This notion of t_{drift} leads to Eq. (VI.5), too, but with q replaced by $-q > 0$.

VII. CONSISTENCY OF THE APPLIED APPROXIMATIONS

Once a solution for the boundary-value problem formulated by Eqs. (1-3) is known, one can check *a posteriori* the consistency of the underlying simplifying approximations.

- First, our model assumes that the spatial distribution of the generated chemical species is approximately stationary and undistorted by the Marangoni flow. The relevance of the advection by this flow is quantified by the Peclet number⁴ for the number density field $c(\mathbf{x})$: perturbations on the relevant length scale L evolve by diffusion on a time scale⁴ $\propto L^2/D_+$, while the time scale associated with advection is $\propto L/|\mathbf{u}(L)| = 2t_{\text{drift}}(L)$ (see Eq. (9) in the main text and Eq. (VI.3)). This leads to a Peclet number Pe_{chem} as the ratio of these two time scales. By using Eqs. (VI.4) and (VI.5) one obtains

$$\text{Pe}_{\text{chem}} = \frac{L^2/D_+}{2t_{\text{drift}}} = |q| \frac{D_p}{D_+}. \quad (\text{VII.1})$$

⁴ Here we use the “mean” diffusion coefficient D_+ for the purpose of providing a simple estimate of the order of magnitude of this time scale.

A small value of this ratio of time scales indicates that the assumption that $c(\mathbf{x})$ is a stationary field determined by diffusion (compare Eq. (1) in the main text) is well grounded. Typically one has $D_p \ll D_+$: a micron-sized particle exhibits $D_p \sim 10^{-13} \text{ m}^2/\text{s}$, whereas $D_+ \sim 10^{-4} - 10^{-9} \text{ m}^2/\text{s}$ for the experimental set-ups discussed in the main text. Thus, even though the parameter $|q|$ can be large (see the discussion on the value of $|q|$ in the main text), Pe_{chem} is small for colloidal particles. In the case that D_p becomes comparable to D_+ (e.g., for nanoparticles and liquid-liquid interfaces) the range of values of q , for which the assumption of a diffusion-dominated stationary profile of $c(\mathbf{x})$ is expected to hold, is somewhat reduced.

• Another simplifying assumption is that of a flat fluid interface. We can derive an order-of-magnitude estimate of the actual interfacial deformation as follows. Upon integrating Eq. (III.3a) over an infinitesimal cylindrical box which has the axis aligned with the interface normal \mathbf{e}_z , and by using Gauss' theorem, one obtains

$$\left[\overset{\leftrightarrow}{\sigma} \Big|_{z=0^+} - \overset{\leftrightarrow}{\sigma} \Big|_{z=0^-} \right] \cdot \mathbf{e}_z = -\nabla_{\parallel} \gamma - \mathbf{e}_z \phi. \quad (\text{VII.2})$$

From this with $\mathbf{e}_z \cdot \nabla_{\parallel} \gamma = 0$ and the relationship $H = \phi/(2\gamma)$ for the constraining force ϕ , it follows that the mean curvature H is determined by discontinuity in the normal stress at the interface:

$$H = -\frac{1}{2\gamma} \mathbf{e}_z \cdot \left[\overset{\leftrightarrow}{\sigma} \Big|_{z=0^+} - \overset{\leftrightarrow}{\sigma} \Big|_{z=0^-} \right] \cdot \mathbf{e}_z. \quad (\text{VII.3})$$

The velocity field $\mathbf{v}(\mathbf{x})$ given by Eq. (III.3) can be written as the sum $\mathbf{v}(\mathbf{x}) = \mathbf{u}(\mathbf{x}) + \mathbf{w}(\mathbf{x})$ of the Marangoni flow $\mathbf{u}(\mathbf{x})$ defined by Eq. (5) in the main text and a perturbation $\mathbf{w}(\mathbf{x})$ thereof induced by the particle. The Marangoni flow can be shown to solve the following boundary-value problem [4]:

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla \cdot \overset{\leftrightarrow}{\sigma}_u = -\delta(z) \nabla_{\parallel} \gamma, \quad \text{if } \mathbf{x} \in \mathcal{D}, \quad (\text{VII.4a})$$

$$\mathbf{u}(\mathbf{x}) \text{ continuous everywhere}, \quad (\text{VII.4b})$$

$$\mathbf{e}_z \cdot \mathbf{u} = 0 \text{ at the interface}, \quad (\text{VII.4c})$$

$$\mathbf{u}(|\mathbf{x}| \rightarrow \infty) = 0, \quad (\text{VII.4d})$$

$$\overset{\leftrightarrow}{\sigma}_u(\mathbf{x}) := \eta(\mathbf{x}) \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger \right] - p_u \mathcal{I}. \quad (\text{VII.4e})$$

We note that in Eq. (VII.4a) no vertical force $\mathbf{e}_z \phi$ due to the Laplace pressure appears. Therefore, the Marangoni flow does not deform the interface and the constraint of a flat interface is actually exact.

The equations obeyed by the perturbation $\mathbf{w}(\mathbf{x})$ are obtained by subtracting Eq. (VII.4) from Eq. (III.3):

$$\nabla \cdot \mathbf{w} = 0, \quad \nabla \cdot \overset{\leftrightarrow}{\sigma}_w = -\delta(z) \mathbf{e}_z \phi, \quad \text{if } \mathbf{x} \in \mathcal{D}, \quad (\text{VII.5a})$$

$$\mathbf{w}(\mathbf{x}) \text{ continuous everywhere}, \quad (\text{VII.5b})$$

$$\mathbf{e}_z \cdot \mathbf{w} = 0 \text{ at the interface}, \quad (\text{VII.5c})$$

$$\mathbf{w}(\mathbf{x}) = \mathbf{V} - \mathbf{u}(\mathbf{x}), \quad \text{if } \mathbf{x} \in \mathcal{S}_p, \quad (\text{VII.5d})$$

$$\mathbf{w}(|\mathbf{x}| \rightarrow \infty) = 0, \quad (\text{VII.5e})$$

$$\overset{\leftrightarrow}{\sigma}_w(\mathbf{x}) := \eta(\mathbf{x}) \left[\nabla \mathbf{w} + (\nabla \mathbf{w})^\dagger \right] - p_w \mathcal{I}. \quad (\text{VII.5f})$$

Therefore, a possible interfacial deformation can be described completely in terms of the perturbation field $\mathbf{w}(\mathbf{x})$ (compare Eq. (VII.3)):

$$H = -\frac{1}{2\gamma} \mathbf{e}_z \cdot \left[\overset{\leftrightarrow}{\sigma}_w \Big|_{z=0^+} - \overset{\leftrightarrow}{\sigma}_w \Big|_{z=0^-} \right] \cdot \mathbf{e}_z. \quad (\text{VII.6})$$

The field $\mathbf{w}(\mathbf{x})$ is not identically zero only because the particle has a finite spatial extent: in the point-particle limit $R/L \rightarrow 0$, one obtains $\mathbf{V} = \mathbf{u}(\mathbf{x}_0)$ (see Eq. (9) in the main text), and the boundary condition in Eq. (VII.5d) reduces to $\mathbf{w} = 0$. Therefore, the origin of the perturbation field is related to the variation of the Marangoni flow on the scale of the particle radius. In the limit $R/L \rightarrow 0$, the order of magnitude of the characteristic velocity scale of the perturbation can be estimated as (compare Eq. (8) in the main text)

$$|\mathbf{w}| \sim |\mathbf{u}(\mathbf{x} \in \mathcal{S}_p) - \mathbf{u}(\mathbf{x}_0)| \propto R \left| \frac{\partial u_z}{\partial z} \right|_{\mathbf{x}=\mathbf{x}_0} \propto \frac{R}{L} |\mathbf{u}(\mathbf{x}_0)|. \quad (\text{VII.7})$$

This leads to the estimate

$$\left| \frac{\partial w_z}{\partial z} \right| \sim \frac{|\mathbf{w}|}{L} \sim \frac{R|\mathbf{u}(\mathbf{x}_0)|}{L^2} \quad (\text{VII.8})$$

because the scale of the spatial variation of \mathbf{w} is L (compare Eq. (VII.7)). Assuming that this provides the correct order of magnitude for the discontinuity at the interface in the normal stress corresponding to the perturbation field $\mathbf{w}(\mathbf{x})$, one obtains from Eqs. (VII.6) and (VII.5f) the order of magnitude estimate⁵

$$|H| \sim \frac{1}{2\gamma} \left(\overset{\leftrightarrow}{\sigma}_w \right)_{zz} \sim \frac{1}{2\gamma} \eta_+ \left| \frac{\partial w_z}{\partial z} \right| \sim \frac{\eta_+ R |\mathbf{u}(\mathbf{x}_0)|}{2\gamma L^2}. \quad (\text{VII.9})$$

Using Eq. (9) for the value of $|\mathbf{u}(\mathbf{x}_0)|$ and the definition of q in Eq. (10), one finally arrives at

$$L|H| \sim |q| \frac{k_B T}{12\pi\gamma L^2}. \quad (\text{VII.10})$$

The dimensionless product $L|H|$ quantifies the importance of the interfacial curvature on the relevant length scale L . A small value of $L|H|$ means that the approximation of a flat interface is reliable. With a typical value $\gamma \sim 10^7 k_B T / \mu\text{m}^2$ of the surface tension one has

$$L|H| \sim 3 \times 10^{-9} \times |q| \left(\frac{\mu\text{m}}{L} \right)^2. \quad (\text{VII.11})$$

This is indeed a small quantity even if $|q|$ is as large as 10^4 (see the discussion on the value of $|q|$ in the main text).

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⁵ We use the arithmetic mean η_+ for the purpose of providing a simple estimate of the order of magnitude of the viscosity.